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Multifunctional Hydrocarbon Cleaning Package: Removing, Degrading, and Protecting

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ABSTRACT

Removal and proper disposal of hydrocarbon pollutants is increasingly becoming a task we have to face in our daily lives. From disastrous large scale oil spill, to everyday small accidental leakage at garage or gas station, to cleaning grease off metal parts in metal working industry, an efficient, cost effective and environment-friendly cleaning solution for hydrocarbon contamination is desired. The ideal products would allow a user to remove hydrocarbon contaminants and easily dispose of the waste in a manner that meets environmental regulation requirements. In the case of metal working applications, a cleaning product that protects the parts from corroding after grease removal will greatly increase productivity. The products discussed in this paper perform multifunctional duty of removing hydrocarbon and degrading them in a single package utilizing hydrocarbon degrading bacterium. In addition, the products for metal working application provide corrosion protection to the cleaned metal parts. Three products were evaluated: a soil bio-remediator, and two degreasers. The test results show that the soil remediator had a 60% reduction of hydrocarbons in contaminated soil vs an untreated, using Gas Chromatography/Mass Spectrometry with a modified EPA Method 8270. The degreaser products exhibited grease removal effectiveness of up to 95% according to ASTM G-122. The compatibility between the corrosion inhibitor and the microbes in the degreaser was studied by measuring microbial viability in cell cultures. The degreasers provided corrosion protection of 90-95% according to ATSM G31.

INTRODUCTION

Petroleum oil contamination is becoming increasingly common as our use of hydrocarbons increases, from disastrous large scale oil spills to vehicles leaking oil. US EPA classified petroleum hydrocarbon as a priority environmental pollutant in 1986. In 2013 alone, the quantity of oil spilled was over 7000 tonnes[1]. With fracturing technology, more and more oil explorations are occurring near urban centers in this country. A lot of this oil is being transported in aging pipelines and railroad trains. More pipeline constructions have been proposed, and are met with considerable opposition out of environment concerns. It is inevitable that the need for cleaning oil spills on land will increase [2].

Cleanup of oil spills and disposal of residue hydrocarbon generated from industrial processes, has been of great concern because of the environmental damage they can cause. Many government agencies impose regulations for the disposal of petro hydrocarbons [3,4]. Strategies for controlling environmental contamination by petroleum and its derivatives have been the subject of various studies over the past three decades[5].

Bioremediation is one of the most popular remediation technologies for soils contaminated with petroleum hydrocarbons[6]. Biological treatments are advantageous over physicochemical methods as they are cost effective, efficient and environmentally friendly[7]. Bioremediation works through bioaugmentation, which adds microorganisms to naturally occurring microbial species, and biostimulation. Biostimulation enhances the environmental conditions such as pH, nutrients, and aeration, to create the optimum environment for the bacteria to degrade hydrocarbons. Through these two arms, bioremediation has the benefits of high treatment efficiency, low cost, and compatibility with other techniques[8]. The effectiveness of microorganisms as agents in the destruction and recycling of organic matter in the biosphere is widely acknowledged[9]. Bioremediation enables the conversion of organic waste into sludge (microbial cells and minerals), but a great portion of the waste is converted into carbon dioxide, water and other end products[10, 11]. Numerous genera of bacteria are found to be beneficial in hydrocarbon degradation and most of them belong to *Bacillus; Pseudomonas* and *Arthrobacter* species[12, 13, 14].

In metal working industry, the ideal cleaning product would allow a user to remove hydrocarbon effectively and subsequently dispose of the waste easily in a manner that meets environmental regulations. It also requires protection of the cleaned metal parts from corrosion before their further processing procedure[15].

Discussed in this paper are three products that provide "green" hydrocarbon cleaning solutions. A number of naturally occurring, environmentally safe, and non-pathogenic bacteria culture were selected to give Products A, B, and C their ability to degrade hydrocarbon. The bacteria selected belong to three main genera including *Bacillus sp., Pseudomonas sp.,* and *Arthrobacter sp.* The bacteria have been selected for their production of a wide range of intracellular and extracellular enzymes essential to degrade organic compounds including proteins, carbohydrates, fats, oils, greases and other recalcitrant organic substances. In addition, the finished products A, B and C have been formulated with bio-stimulants (nutrients and growth factor) to maximize bacteria metabolic activities and viable cell count.

Product A is a soil bioremidiation product that cleans soil contaminated with petroleum and related wastes. Product B and Product C are both multifunctional degreaser/corrosion preventative packages that remove hydrocarbon pollutants from metal or concrete surfaces, degrade the removed hydrocarbon in the waste, and protect the cleaned metal parts from corrosion.

Product A can be applied to soil easily with any appropriate fertilizer or seed spreading equipment. Dry or wet application can both be used. Gas chromatography-mass spectrometry analysis, based on EPA Method 8270[16], was carried out to examine the amount of hydrocarbons in contaminated soils before and after the treatment. The results show that the treatment resulted in a 60% reduction of hydrocarbons in contaminated soil vs the untreated. Product A offers a more economical and cost effective approach compared to other treatments such as landfill, chemical extraction, electro-reclamation, and incineration.

Product B and Product C are formulated with surfactants, corrosion inhibitors, and bio-remediation agents. Product B exhibits grease removal effectiveness of 95% according to ASTM[(1)] G-122[17] testing. It also provides excellent degreasing to contaminated concrete surfaces. Product C provides 95% corrosion protection compared to conventional degreasers following ASTM G31[18] standard.

EXPERIMENTAL PROCEDURE

Growth Characteristics of the Bacteria Selected
The optimum environment for hydrocarbon degradation for the bacteria in Products A, B and C is shown in Table 1.

Table 1
Environmental Conditions for
Bioaugmentation with Product A, B, and C

Parameter	Effective Range	Optimum range
pH	5.0 – 9.0	6.5 – 7.5
Temperature	10 – 50 °C	20 – 30 °C
Salinity	0 – 5%	0.5 – 2 %
Dissolved Oxygen	>1.0 ppm	1 – 10 ppm

Bioremediation of Contaminated Soil with Product A
Soil contaminated by hydrocarbons was created by adding #2 diesel (5% by weight) to a commercial garden potting soil. The contaminated soil was piled 2" (5.08cm) high in 2 separate 1 gallon containers. One would receive bioremediation treatment Product A; one would be untreated (control). Before each inoculation, a mixture of 2.5% Product A in water was freshly prepared. The preparation was let to stand at room temperature for 3 hours to allow the microbial materials to be activated. This mixture was then dripped into the soil and mixed thoroughly at a rate of 2% by weight. The inoculations were carried out weekly for 3 weeks. The control soil received same amount of deionized water at the corresponding time. The soil was stirred daily to facilitate aeration.

([1]) ASTM International, 100 Barr Harbor Dr., PO Box C700, West Conshohocken, PA, 19428

Extraction of Hydrocarbon from Contaminated Soil

The hydrocarbon was extracted from the contaminated soil using a method based on *Extractable Petroleum Hydrocarbons Methodology* by New Jersey Department of Environmental Protection, Site Remediation Program, version 3.0[19] (based on USEPA Method 8270). Briefly, in this method, hydrocarbons in contaminated soil were extracted with methylene chloride. The resulting methylene chloride extract was analyzed using Gas Chromatography/Mass Spectrometry (GC/MSD) for the presence of petroleum hydrocarbons.

8g of soil was placed into a 2-neck round bottom flask together with 8g sodium sulfate, 100ml methylene chloride, and a stir bar. The extraction was carried out in a 39˚C water bath and was fitted with a condenser cooled by tap water. At the end of 3 hour extraction, the mixture was allowed to cool and settle. The liquid was filtered with a 0.45um PTFE filter and saved for GC analysis.

Gas Chromatography/Mass Spectrometry Detection(GC/MSD) Analysis

The analysis was based on EPA Method 8270. The following equipment and parameters were used:
Agilent[†] 8720 Gas Chromatography/5970C Mass Spectrum Detector
HP[†]-5ms capillary column (30mx0.25mmIDX250um)
Carrier gas: Helium, 1ml/min constant gas flow
Injection: 1ul, 18:1 split, 260C
Oven program: 40 C for 3 min; to 270C at 10C/min; final hold 5 min
MSD setting: TIC scan, 40-550 amu

Evaluating Effectiveness of Cleaning Agents on Steel

The standard of ASTM G-122 (Test Method for Evaluating the Effectiveness of Cleaning Agents) was used to evaluate the cleaning effectiveness Product B and Product C. The weight of a cleaned 3x5 inch carbon steel SAE 1010 panel was recorded. The panel was then coated with 12 drops of complex hydrocarbons (Hyprene 100[†] by Ergon Refining[†] , Inc) (a Hydro-treated heavy Naphthenic) on one side. The panel was allowed to dry overnight so the hydrocarbon could build up on the panel. The weight of the contaminated panel was recorded. Then, 6ml of a 25% Product B solution was applied evenly to the contaminated surface, and was allowed to sit on the surface for 10 minutes. The panel was then submerged in agitated water (23˚C, in a filled 4L beaker agitated with a large Cowles[†] blade at 400 rpm) for 30 seconds, and taken out of the water tank and hung from a plastic coated wire hook to dry overnight. Weight of the dried, cleaned panel was recorded. The control was an uncontaminated panel subjected to the same cleaning procedure. The test was run in triplicate. The % cleaning efficiency was calculated using the following formulas:

$$CM = CMTP - CCP$$

$$\% \ CE = 1 - 100 \ x \ CM \ /IC$$

Where CM - Contaminate remaining

CMTP - contaminate remaining on a test panel
CCP - contaminate incurred on the control panel during cleaning process
IC – initial contaminate
% CE - cleaning efficiency

Evaluating Effectiveness of Cleaning Agent on Concrete Surface

2 mL of used motor oil was brushed onto the surface of a concrete puck. The puck was baked at 66°C for 4.5 hours and then allowed to sit at ambient temperature overnight. Half of the contaminated surface was treated with Product B and the other half with water (control). A tape was placed in the middle of the puck surface to separate the two areas. 5ml of Product B was spread evenly on the treatment side. After 5 minute contact, the surface was brushed with a toothbrush and rinsed with water. On the control side, the surface was brushed with toothbrush for 1 minute and then rinsed.

Evaluating Corrosion Protection

The standard of ASTM G-31 (Standard Guide for Laboratory Immersion Corrosion Testing of Metals) was used to evaluate corrosion protection. Cleaned carbon steel panel (Cold rolled SAE1010 carbon steel by Q-Lab Corporation[†]) was subjected to immersion and partial immersion tests in the multi-function cleaning solution Product B or Product C at various concentrations. The controls were the comparable cleaning solutions but without the presence of corrosion inhibitor. Weight loss method was used to assess the protection (%Z) in immersion test. Visual inspection and photo record were used to assess the protection in partial immersion test.

$$\%Z = 100 \times (C_c - C_i)/C_c$$

where C_c - weight loss without inhibitor
C_i - weight loss with corrosion inhibitor
Z = Corrosion Protection

RESULTS AND DISCUSSIONS

Stability of the Bacteria Culture in Product B and Product C

The bacteria blend has been shown to be compatible with both chemical surfactant and corrosion inhibitor by plate count method on trypticase soy agar (TSA) medium. After six months of storage at 30°C, the loss of cell viability in both Products B and C was less than 10%, Figure 1.
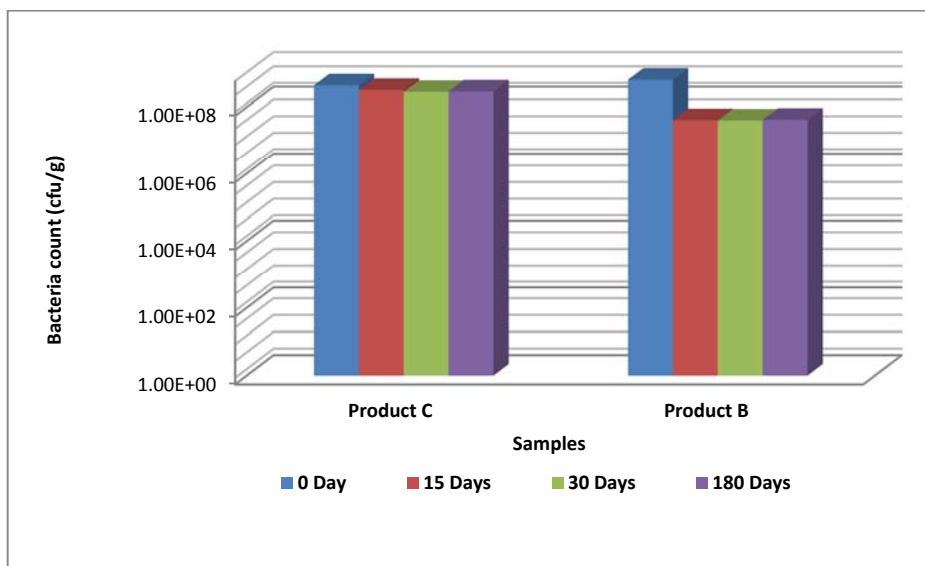

[†] Trade name

Figure 1: Stability of the Bacteria blend in Product B and Product C

Effect of Bioremediation by Product A on Hydrocarbon Contaminated Soil

GC/MSD analysis of the Methylene Chloride extracts shows that after one treatment by Product A, the amount of hydrocarbon in the treated soil is much reduced than the untreated soil, Figure 2.
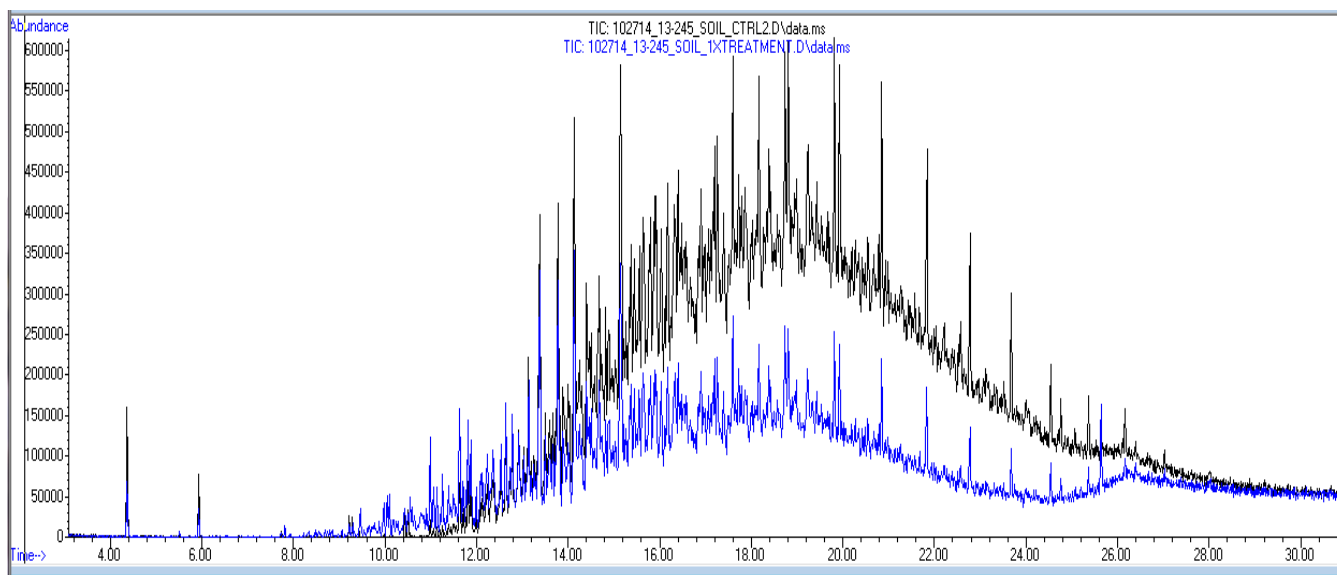

**Figure 2: Chromatograms of Methylene Chloride Extract of Contaminated Soil
After one Treatment of Product A (blue) vs. the Untreated (black)**

Further treatments by Product A further reduced those hydrocarbons with retention time in the range of 10 min to 18 min, mostly of aromatic nature, Figure 3.
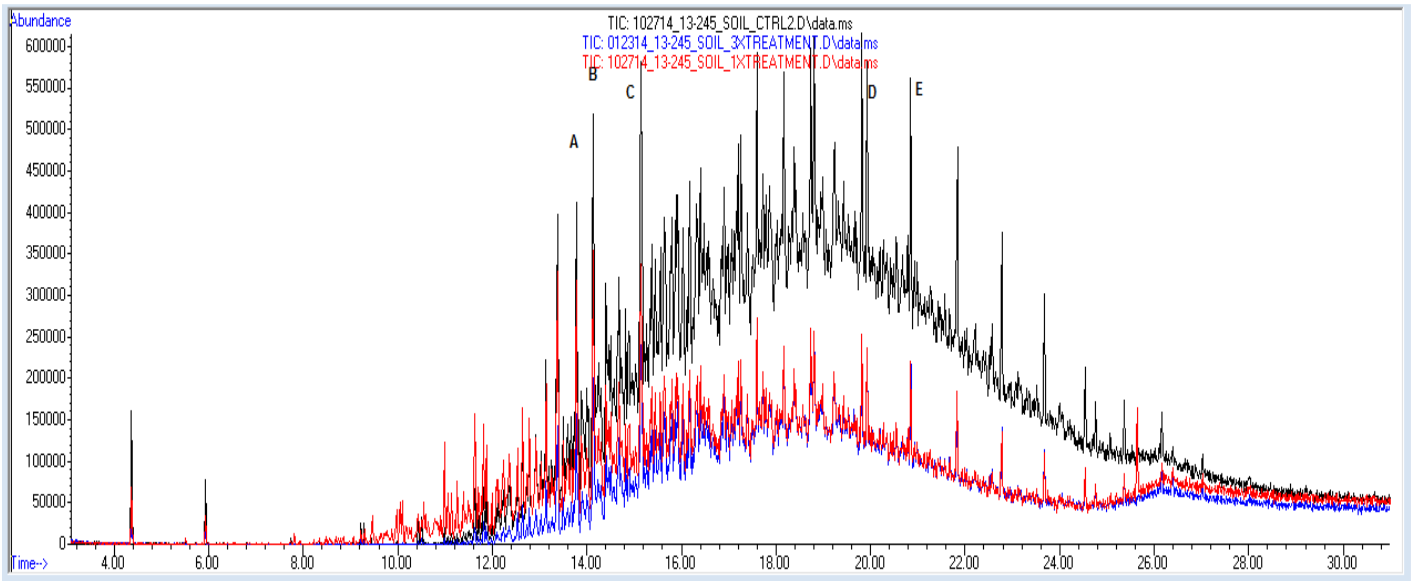
Figure 3: Chromatograms of Methylene Chloride Extract of Soil after 1X Treatment (red), 3X Treatments of Product A(blue), and Untreated (black)

Calculation on the reduction in selected peak areas indicates that 1X treatment by Product A reduced aromatic hydrocarbons in the soil by 24% while 3X treatments by 60% vs. the untreated soil. For the later eluting hydrocarbons, the 1X treatment reduced hydrocarbons 30-60% vs. the untreated, depending on the hydrocarbon compounds, Table 2.

Table 2
Reduction of Hydrocarbon in Contaminated Soil
after 1X and 3X Treatments of Product A

Peak	Retention Time (min)	Compound	%Reduction after 1X Treatment vs. the Control	%Reduction after 3X Treatments vs. the Control
A	13.779	C11 aromatic	24%	60%
B	14.132	C12 aromatic	9%	56%
C	15.144	C16 alkane	46%	57%
D	19.824	C17	31%	34%
E	20.854	C20s	59%	60%

Cleaning Effectiveness of Parts Washer Product B

Evaluation based on ASTM G-122 shows that 94.83% of hydrocarbons contaminate on a carbon steel panel was removed by Parts Washer Product B. In comparison, water alone only removed 45% of the contaminant, Table 3.

Table 3
Cleaning Efficiency of Product B on Contaminated Carbon Steel Panel (ASTM G-122)

Cleaning Liquid	Panel Weight	Panel Weight + Contaminate	Weight of contaminate	Panel Weight after cleaned and dried	Contaminate remaining after cleaning	% cleaning efficiency	% cleaning efficiency (average of 3)
25% Product B In DI water	60.9085g	61.2380g	0.3295g	60.9300g	21.5mg	93.96%	94.83%
	60.1057g	60.4254g	0.3197g	60.1264g	20.7mg	94.03%	
	59.6312g	59.9380g	0.3068g	59.6435g	12.3mg	96.51%	
	59.4954g	0 contaminate (control)	-	59.4970g	1.6mg	-	-
DI water	60.0990g	60.4252g	0.3262g	60.2801g	181.1mg	44.48%	45.14%
	59.8183g	60.1300g	0.3117g	59.9885g	170.2mg	45.40%	
	59.4930g	59.7905g	0.2975g	59.6550g	162.0mg	45.55%	

Testing on concrete surface indicates that Product B also effectively removed hydrocarbon contaminates on concrete surface, Figure 4.

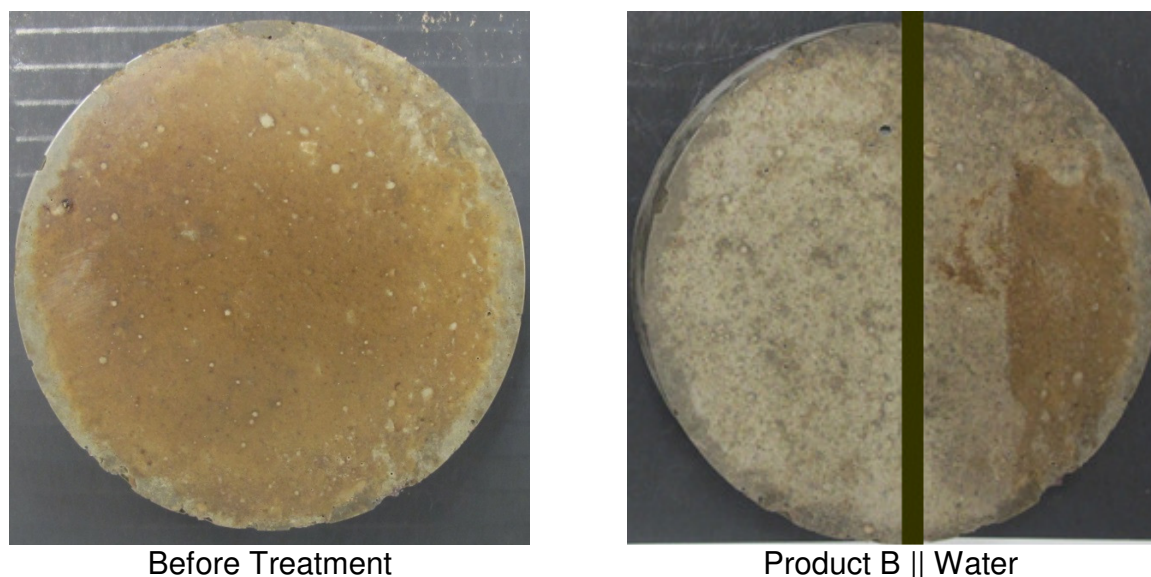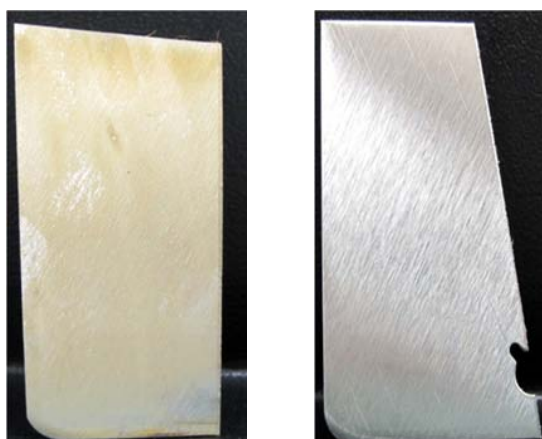Before Treatment   Product B || Water

Figure 4: Cleaning Motor Oil-Contaminated Concrete Surface using Product B

Corrosion Protection
Immersion Test shows that the inhibitor-containing cleaners Product B and Product C provided 95% and 90% corrosion protection to carbon steel, respectively, Table 4. Partial Immersion Test shows that Product C provided excellent protection to carbon steel in liquid phase, in vapor phase, and at liquid/vapor interphase, Figure 5.

Table 4
Corrosion Protection for Carbon Steel after Immersion Test with Products B and C
(ASTM G 31)

Cleaning Liquid	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	% Protection (Z)
10% Control 1 (degreaser, no inhibitor)	15.2420	14.1925	1.0495	-
10% Product B	14.2655	14.1985	0.067	95
5% Control 2 (degreaser, no inhibitor)	12.1479	11.8243	0.3236	-
5% Product C	12.2678	12.2382	0.0296	90

5% Cleaner w/o inhibitor   5% Product C

Figure 5: Protection to Carbon Steel by Product C after Partial Immersion Test

Effect of Bioremediation by Product B on Wastewater from Garage Cleaning
Wastewater collected from cleaning garage floor using Product B was incubated at 30°C under orbital stirring. At least 30% of the total hydrocarbon in the wastewater was removed after 40 hours by the bacteria. The quantity of the BTEX (benzene, toluene, ethyl benzene, xylene) compounds was significantly reduced after one week of treatment, Table 5.

Table 5
Bioremediation Rates of Hydrocarbon in Wastewater from Garage Floor
Cleaned with Product B

Contaminant	Initial Conc. (ppm)	Final Conc. (ppm)	% Reduction	Degradation Rate (mg/L/hr at 106 cfu/ml)	Test Period (hours)
Total hydrocarbon compounds	2,000	1,400	30%	15	40
Ethyl benzene	3	0	100%	0.02	170
Toluene	99	15	85%	0.5	170
Xylene	3.6	0.4	89%	0.02	170
Phenol	90	0	100%	1.9	50
Methylene Chloride	15	0	100%	0.09	170

CONCLUSIONS

According to national testing standards, the soil bioremidiator Product A reduced the petroleum hydrocarbon in contaminated soil by 60% after 3 weeks. Following these standards, it was demonstrated that degreaser, corrosion inhibitor, and beneficial bacteria can be synergistically combined to create a multifunctional degreaser and corrosion preventative package. This multifunctional package increases productivity by removing unwanted hydrocarbons and subsequently degrading them in the waste, all the while providing corrosion protection to the cleaned metal parts.

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