



ENVIRONMENTAL POLLUTION ANALYSIS PRODUCED BY LOW-PRESSURE COLD PLASMA IN THE SHEET METAL CLEANING PROCESS

ANÁLISIS DE LA CONTAMINACIÓN AMBIENTAL PRODUCIDA POR EL PLASMA FRÍO DE BAJA PRESIÓN EN LA LIMPIEZA DE LÁMINAS METÁLICAS

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Abstract

The present research addresses an analysis of the level of contamination produced by gases generated from carbon monoxide (CO), carbon dioxide (CO₂) and hydrocarbons (HC) in the cleaning of metallic sheets of stainless steel AISI / SAE 304, when applying low pressure cold oxygen plasma for the removal of oils ISO 32, ISO 68 and ISO 220, using different generator control parameters according to the lubricating oil removed from the surface of the stainless steel metallic sheet. The experimentation was carried out in a first phase in which a discharge was applied directly to the surface of the sheet contaminated with a volume of 0.1 ml of oil, and in a second phase in which the sheet with the oil was immersed in an oil degreaser to perform a pre-cleaning prior to the application of low pressure cold plasma on the surface. For analyzing the results in the level of gases generated by each oil, a statistical analysis is applied to determine if there is a significant difference in the level of the gases generated between the two phases.

Keywords: Low pressure cold plasma, contamination.

Resumen

La presente investigación aborda un análisis del nivel de contaminación producido por los gases generados de monóxido de carbono (CO), dióxido de carbono (CO₂) y los hidrocarburos (HC) en la limpieza de láminas metálicas de acero inoxidable AISI/SAE 304 aplicando plasma frío de oxígeno a baja presión para la remoción de los aceites ISO 32, ISO 68 e ISO 220, con diferentes parámetros de control del generador de acuerdo con el aceite lubricante removido de la superficie de la lámina metálica de acero inoxidable. La experimentación se realizó en un primer proceso con una descarga aplicada directamente a la superficie de la lámina impregnada con el aceite colocando con un volumen de 0,1 ml y en un segundo proceso donde la lámina con el aceite impregnado fue sumergida en un desengrasante para aceites y grasas con la finalidad de realizar una limpieza previa a la aplicación del plasma frío a baja presión en la superficie. Para el análisis de los resultados en el nivel de gases generados por cada aceite se aplica un análisis estadístico para determinar si existe una diferencia significativa en el nivel de los gases generados en las dos etapas.

Palabras clave: Plasma frío a baja presión, contaminación.

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1. Introduction

In the production processes it is sought to eliminate or reduce emissions, dumping and wastes with an efficient use of the resources, and technologies that enable to yield the requirements and specifications of a product with the smallest environmental impact [1].

The contamination produced by the pickling baths in the cleaning of metallic sheets with acids and bases, considered toxic, harmful and hazardous for health, infrastructure and environment has considerably increased in recent years. Heavy metals such as zinc, chromium and copper that accumulate in the pickling baths are theoretically considered as suspended substances, and constitute another problematic due to the serious environmental contamination they produce [2–5].

At present, several superficial cleaning processes are carried out to reduce or eliminate the contamination, as new alternatives to traditional processes. They show the same efficiency, considering that the presence of impurities or remains of oils and greases in the different surfaces to be cleaned will decrease adherence in further superficial treatments [6, 7].

According to previous studies, the application of low-pressure cold plasma exhibits satisfactory results in removing oils from metallic sheets using non-pollutant gases, with the purpose of removing both mechanical and organic compounds [8]. The adhesive properties of the material will depend upon the effectiveness of this treatment according to the contact angle, which is directly related to the free superficial energy [9–11].

The superficial cleaning of organic compounds using low-pressure cold plasma, is a method that bombards ions of a particular gas, which is produced by physical effects or chemical reactions, to transform the substances that are on the metallic sheets to the gaseous phase, thus expelling them from the chamber to the atmosphere [12]. Previous research works [6, 13] indicate that the application of cold plasmas in certain industrial processes is more efficient and less expensive, thus reducing the contamination and toxic residues. The cleaning process is more efficient, since it reduces the contact angle when previously immersed in a degreaser [8] (Figure 1).

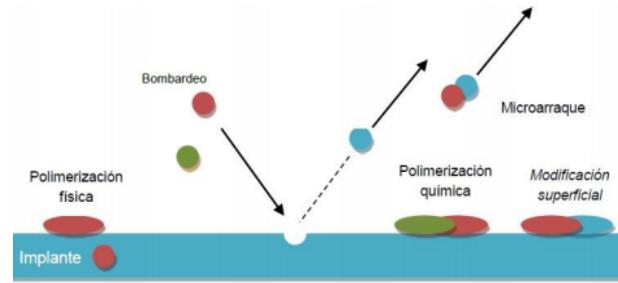


Figure 1. Modifying effects on the surface of the plasma [14].

The angle of contact is a superficial property of the solids, which quantifies its tendency to the hydrophobicity, as an important parameter to analyze the mechanisms of interaction between the solid and liquid phases that appear in many industrial operations. The value of the angle of contact mainly depends on the relation between the adhesive forces of the liquid and the surface, and the internal forces of cohesion of the liquid itself. As the interaction gets smaller, the angle of contact is larger and its value is directly related with the quality of the cleaning, i.e. a smaller angle of contact results in a greater wettability, indicating a smaller presence of contaminant agents in the surface under study; it is considered that values smaller than 30° will show high degree of cleanliness, and that the surface will be ready for further coverings. For rugged surfaces, is it important to determine the apparent angle θ_{ap} , and if the surface has an inclination, the intrinsic angle θ_i [8, 15, 16] (Figure 2).

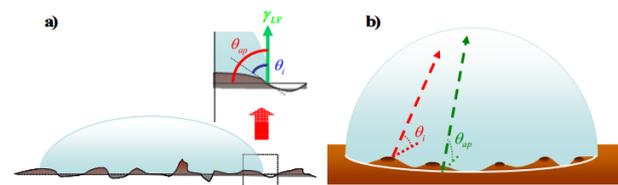


Figure 2. Intrinsic and apparent contact angle on a surface a) Rugged and homogeneous b) Smooth and heterogeneous [16].

2. Materials and methods

2.1. Materials

2.1.1. Stainless steel sheets

Stainless steel sheets AISI/SAE 304 of dimension 7 x 7 cm and thickness of 2 mm were used in the research for laboratory tests, as shown in Figure 3. The sheets were impregnated with 0,1 ml of the lubricant oils ISO 32, ISO 68 and ISO 220, previous to the discharge of the oxygen plasma. The rugosity of the surface of the steel was not considered, since it does not have

influence on the effect of the ionized oxygen gas on the controlled volume of oil deposited on the surface.



Figure 3. Stainless steel sheet.

2.1.2. Lubricant oils

The lubricant oils ISO 32, ISO 68 and ISO 220 were utilized as contaminant agents, and placed on the surface of the stainless steel sheets. Such oils were provided by the commercial house Gulf, and have the properties shown in Table 1.

Table 1. Properties of lubricant oils

Oils	Viscosity cSt/40 °C	Density to 15 °C kg/l	Flammability Point °C
ISO 32	32	0,87	202
ISO 68	68	0,88	218
ISO 220	220	0,89	256

2.1.3. Oxygen

High purity oxygen provided by the company AGA, was utilized for generating the ionized gas or plasma. The output pressure of the tank is 1 bar, which was regulated in the plasma generator equipment, according to the stated experimental conditions.

2.1.4. Low-pressure cold plasma generator

The brand of the plasma generator equipment utilized here is Diener, as shown in Figure 4. In this equipment, the neutral particles and the ions arise between 25 and 100 °C, with an electronic temperature between 105 °C and 5000 °C by means of continuous current and pressures below 133 mbar. The equipment is semi-automatic, where three different gases for generating plasma can be used, and pressure, time and power parameters can be controlled [17].



Figure 4. Plasma generator.

The vacuum plasma chamber can be seen in Figure 5, where the stainless steel sheets impregnated with oil are placed. In addition, it comprises a vacuum pump with rotating paddles of two stages, has a residual pressure close to zero and enables the ventilation of the chamber

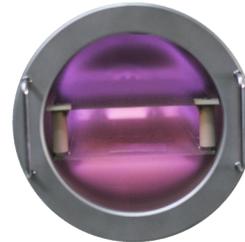


Figure 5. Plasma chamber.

Table 2 contains the parameters established in the oxygen plasma generator equipment that, according to research studies carried out by [8], are suitable for cleaning metallic sheets with low-pressure cold plasma.

Table 2. Parameters of the plasma generator

Processes	Lubricants	Control parameters.		
		Time (min)	Pressure (mbar)	Power (%)
Processes with immersion	ISO 32	10	0,26	90
	ISO 68	10	0,30	90
	ISO 220	15	0,32	90
Processes without immersion	ISO 32	15	0,28	90
	ISO 68	15	0,32	90
	ISO 220	20	0,34	90

2.1.5. Gas analyzer

The level of gases generated in the cleaning of stainless Steel sheets were detected by the QROTECH gas analyzer, model NGA 6000, shown in Figure ???. This analyzer is capable of detecting (i) carbon monoxide, in the measuring range 0.00 to 0.99 %, which is highly toxic and can cause death when present at

high levels, (ii) carbon dioxide in the range 0.0 to 20.0 % that affects global warming, (iii) diatomic oxygen in the range 0.00 to 25.00 %, that does not affect the environment, (iv) hydrocarbons in the range 0 to 20000 ppm, combinations of carbon and hydrogen commonly responsible for intoxications, and (v) NO_x in the range 0 to 5000 ppm, which are reactive, such as nitric oxide (NO) and nitrogen dioxide (NO₂), and very harmful for health, environment and structures [18,19].



Figure 6. Gas analyzer.

2.1.6. Digital optical goniometer

The KSV CAM100 optical goniometer shown in Figure 7, was utilized to determine the angle of contact of the test liquid on the metallic surface. It incorporates a camera CCD (charged-coupled device) with an optic of 50 mm, and the software CAM 100 for image treatment. A volume of 5 μ l of test liquid was utilized for measuring the angle of contact.



Figure 7. Digital goniometer.

2.1.7. Test liquid

Distilled or demineralized water was used as test liquid, with the components of the free superficial energy that are shown in Table 3.

Table 3. Components of the test liquid [20].

Test liquid	Energy of the surface (γ)	Dispersive component (γ^d)	Polar componente (γ^p)
Distilled water	72.80	21.80	51.00

The components of the liquid obtained by means of the angle of contact with distilled water, enable the calculation of the free superficial energy using the theories of Fowkes and Wu.

2.2. Methods

2.2.1. Statistical methods

Five samples of stainless steel sheets impregnated with the oils ISO 32, ISO 68 e ISO 220, were utilized in this research for analysis in the laboratory. The gases were detected in parts per million (ppm) and percentage (%) as measurements of concentration, with no influence of the quantity or volume of oil on the surface. An analysis of variance (Anova) or hypotheses test was applied to determine if there exists a difference in the percentages and part per million of the generated gases in the cleaning with low-pressure cold plasma, to contrast if the mean percentages of carbon monoxide and carbon dioxide and the parts per million of hydrocarbons, are equal with and without immersion in the degreaser; the gas with the greater contamination was further analyzed.

$$H_0 : \mu_1 = \mu_2$$

There is no difference between the levels of gases

$$H_1 : \mu_1 \neq \mu_2$$

There is a difference between the levels of gases

2.2.2. Process

A micropipette was used to place the contaminant oil for impregnating on the surface. As indicated in Figure 8, the tests to determine the contamination level according to the degree on cleanliness, were conducted out with and without immersion in the dissolvent of the test tube, prior to the application of the cold plasma.



Figure 8. Experimental procedure.

A pre-degreasing was carried out with an immersion in a solvent during 3 minutes, according to the quantity of oil to be removed in the lab test. In industrial treatments for cleaning AISI/SAE 304 steel, it is recommended from 30 to 60 minutes to eliminate organic compounds and remove inorganic compounds that may be present on the surface. Table 4 shows the

properties of the used degreaser [21].

Table 4. Properties of the dissolvent [8].

Property	Value
Density	0,8 g/cm ³
Fusion temperature	-34 °C
Biling temperature	136 °C
Decomposition temperature	480 °C
Flamability	< 37 °C

3. Results and discussion

Tables 5 and 6 present the levels of gases obtained in the cleaning of the surfaces of the metallic sheets impregnated with oil ISO 32, applying low-pressure cold plasma

Table 5. Values of the angle of contact and levels of gases with ISO 32 without immersion in degreaser

N.	Oil (ml)	Angle of contact	Test liquid (μl)	CO (%)	CO ₂ (%)	HC (ppm)
1		16,76°		0,34	0,1	563
2		16,49°		0,38	0,1	576
3	0,1	17,14°	5	0,37	0,1	553
4		16,24°		0,38	0,1	585
5		17,32°		0,41	0,1	601

Table 6. Values of the angle of contact and levels of gases with ISO 32 with immersion in degreaser

N.	Oil (ml)	Angle of contact	Test liquid (μl)	CO (%)	CO ₂ (%)	HC (ppm)
1		12,92°		0,34	0,1	1031
2		12,25°		0,33	0,1	1028
3	0,1	12,73°	5	0,34	0,1	1049
4		12,86°		0,34	0,1	995
5		12,27°		0,37	0,1	1026

An analysis of variance was carried out among the group of gases, carbon monoxide and hydrocarbons, to determine if there is a difference between the contamination levels of the obtained gases in the processes with and without immersion in the degreaser. The null hypothesis states that there is no difference between the groups analyzed with a level of significance $\alpha = 0.05$, obtaining the results presented in Tables 7 and 8.

Table 7. Single factor ANOVA. ISO 32 (CO)

Percentage of CO					
	Sum of squares	gl	Cuadratic mean	F	Sig.
Inter-grupos	0,003	1	0,003	5,953	0,041
Intra-grupos	0,003	8	0,000		
Total	0,006	9			

Table 8. Single factor ANOVA. ISO 32 (HC)

ppm of HC					
	Sum of squares	gl	Cuadratic mean	F	Sig.
Inter-grupos	506700,1	1	506700,10	1387,269	0,000
Intra-grupos	2922,0	8	365,25		
Total	509622,1	9			

As it can be seen in Tables 7 and 8, the p value (Sig.) is smaller than 0.05, which indicates a difference between the percentages of carbon monoxide and hydrocarbons in the processes with and without immersion in the degreaser, determining that there is a greater contamination when the previous immersion takes place. However, it also presents a better cleanliness, as seen in the values of angle of contact in Tables 5 y 6. The levels of carbon dioxide remained constant in the processes with and without immersion.

Tables 9 and 10 present the levels of gases obtained 563 in cleaning the surface of the stainless steel metallic impregnated with the ISO 68 oil.

Table 9. Values of the angle of contact and levels of gases with ISO 68 without immersion in degreaser.

N.	Oil (ml)	Angle of contact	Test liquid (μl)	CO (%)	CO ₂ (%)	HC (ppm)
1		36,93°		0,50	0,2	1177
2		37,55°		0,50	0,2	1151
3	0,1	36,86°	5	0,48	0,2	1098
4		36,91°		0,49	0,2	1133
5		36,05°		0,37	0,2	1088

Table 10. Values of the angle of contact and levels of gases with ISO 68 with immersion in degreaser.

N.	Oil (ml)	Angle of contact	Test liquid (μl)	CO (%)	CO ₂ (%)	HC (ppm)
1		16,03°		0,39	0,2	2068
2		16,52°		0,45	0,2	2214
3	0,1	16,35°	5	0,44	0,2	2315
4		16,96°		0,49	0,2	2185
5		16,83°		0,50	0,2	2220

An analysis with a confidence level of 95% was carried out, to determine if there is a difference between the contamination levels of the gases generated in cleaning of surface of the stainless steel sheets impregnated with the ISO 68 oil, in the processes with and without immersion in a degreaser liquid. Tables 11 and 12 present the results obtained.

Table 11. Single factor ANOVA. ISO 68 (CO)

Percentage of CO					
	Sum of squares	gl	Cuadratic mean	F	Sig.
Inter-grupos	0,000	1	0,000	0,196	0,670
Intra-grupos	0,020	8	0,003		
Total	0,020	9			

Table 12. Single factor ANOVA. ISO 68 (HC)

ppm of HC	Sum of squares	gl	Cuadratic mean	F	Sig.
Inter-grupos	286702,5	1	2867602,50	621,460	0,000
Intra-grupos	36914,4	8	4614,30		
Total	2904516,9	9			

The result in Table 11 presented a p value (Sig.) of $0.670 > 0.05$, thus the levels of carbon monoxide are the same in the processes with and without immersion in degreaser. On the other hand, Table 12 showed a p value (Sig.) of $0.000 < 0.05$, which indicates that the levels of hydrocarbons are different, showing an increment when a previous immersion is carried out; the levels of carbon dioxide remained constant, as can be seen in Tables 9 and 10.

Tables 13 and 14 include the levels of gases obtained when using low-pressure cold plasma to clean the surfaces of the stainless steel sheets impregnated with ISO 220 oil, in processes with and without prior immersion in a degreaser liquid.

Table 13. Values of the angle of contact and levels of gases with ISO 220 without immersion in degreaser

N.	Oil (ml)	Angle of contact	Test liquid (μ l)	CO (%)	CO ₂ (%)	HC (ppm)
1		71,41°		0,47	0,2	1259
2		71,49°		0,45	0,2	1317
3	0,1	71,16°	5	0,47	0,2	1199
4		71,94°		0,49	0,2	1278
5		71,32°		0,50	0,2	1344

Table 14. Values of the angle of contact and levels of gases with ISO 220 with immersion in degreaser

N.	Oil (ml)	Angle of contact	Test liquid (μ l)	CO (%)	CO ₂ (%)	HC (ppm)
1		20,50°		0,51	0,4	1885
2		20,69°		0,52	0,3	1902
3	0,1	20,93°	5	0,51	0,4	1925
4		20,80°		0,50	0,4	1975
5		20,00°		0,51	0,4	1932

An ANOVA analysis was carried out to determine if there is a difference between the levels of the gases generated in cleaning of surface of the stainless steel sheets impregnated with the ISO 220 oil, with and without immersion in the degreaser. Tables 15 and 16 present the results obtained.

Table 15. Single factor ANOVA. ISO 220 (CO)

Percentage of CO	Sum of squares	gl	Cuadratic mean	F	Sig.
Inter-grupos	0,003	1	0,003	13,442	0,006
Intra-grupos	0,002	8	0,000		
Total	0,005	9			

Table 16. Single factor ANOVA. ISO 220 (HC)

ppm of HC	Sum of squares	gl	Cuadratic mean	F	Sig.
Inter-grupos	1038128,4	1	1038128,40	484,541	0,000
Intra-grupos	17140,0	8	2142,50		
Total	1055268,4	9			

Tables 15 and 16 indicate p values (Sig.) smaller than 0.05, thus it can be stated that there is a difference in the contamination levels when cleaning the surface of the metallic sheet impregnated with the ISO 220 oil, with and without immersion in degreaser before applying the low-pressure cold plasma

Table 17 presents the average of the results obtained in the contamination levels of the generated gases, when applying an oxygen plasma for cleaning the metallic sheets.

Table 17. Summary of the average values of angle of contact and level of generated gases

	ISO 32	ISO 68	ISO 220
<i>WIRH IMMERSIN</i>			
Angle of contact	12,606°	16,538°	20,584°
Percentage of CO	0,344	0,454	0,510
Percentage of CO ₂	0,1	0,2	0,38
Parts per million de HC	1025,8	2200,4	1923,8
<i>WITHOUT IMMERSION</i>			
Angle of contact	16,79°	36,46°	71,464°
Percentage of CO	0,376	0,468	0,476
Percentage of CO ₂	0,1	0,2	0,2
Parts per million de HC	575,6	1129,4	1279,4

4. Conclusions

The cleaning processes in AISI/SAE 304 stainless steel sheets using low-pressure cold plasma, with and without immersion in a degreaser prior to the application of the ionized gas exhibit differences in the levels of expelled gases. According to the average of the results, when removing ISO 32 oil from the surface with low-pressure cold plasma, the previous immersion in a degreaser aids in reducing the angle of contact 25%, which indicates a better quality cleaning of the surface, but the contamination levels show a variation, especially the hydrocarbons significantly increase 78.21% since the oil is removed from the surface together with the remains of degreaser, the level of carbon monoxide decreases 8.5% and the carbon dioxide remains constant. This indicates that for removing the ISO 32 oil it is not necessary a prior immersion, since without it an optimal angle of contact is obtained (less than 30°), and less contamination is generated.

When removing ISO 68 oil it was observed that with an immersion of the metallic sheets in degreaser before applying the cleaning process with low-pressure

cold plasma, the level of hydrocarbons increases 95%, the percentage of carbon monoxide decreases % and the percentage of carbon dioxide remains constant with respect to the values obtained without previous immersion. The angle of contact decreases 54% with a previous immersion in degreaser before discharging the plasma, obtaining optimal values of cleanliness smaller than 30°.

When removing ISO 220 oil from the surface, it was observed an increase in the contamination levels in all generated gases when cleaning the metallic sheets with low-pressure cold plasma, if a prior immersion in degreaser was applied to reduce the angle of contact in 71% with respect to the process without immersion. The parts per million of hydrocarbons increased 50%, the percentage of carbon monoxide raised 7% and the carbon dioxide 90%.

In the cleaning of the surfaces of metallic sheets, the ISO 68 oil showed the greater average contamination in hydrocarbons with 2200.4 ppm at an average angle of contact of 16.53°. The ISO 220 oil showed the greater average contamination of carbon monoxide with 0.51% and of carbon dioxide with 0.38%.

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