# CLEANING LABORATORY EVALUATION SUMMARY

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| SCL #: | 2014 |
| DateRun: | 03/24/2014 |
| Experimenters: | George Liang |
| ClientType: | Cleaner Manufacturer |
| ProjectNumber: | Project #3 |
| Substrates: | Liquid |
| PartType: | Coupon |
| Contaminants: | |
| Cleaning Methods: | |
| Analytical Methods: | Goniometry |
| Purpose: | Determining the active oxygen (AO) content of hydrogen peroxide-based general purpose cleaners |

Experimental Procedure:

Introduction
This document aims to provide instruction and background on the test method for determining the active oxygen (AO) content of hydrogen peroxide-based general-purpose cleaners. In addition, information on the particular cleaners themselves, dilution instructions, etc. will be provided. By performing these tests, it is hoped to gain information on the active oxygen stability of these products once they have been diluted by the end-user.

Test Requirements
-Acetic acid 100% - glacial
-Isopropyl alcohol 70%
-Sodium Iodide solution
-0.1M sodium thiosulfate (other normalities are ok, but Eq. (2), below, will need to be adjusted accordingly)
-Erlenmeyer flasks, stirrers, and other standard lab equipment as needed

Background
ASTM E298 describes a standard method for the assay of organic peroxides. Although the method used here differs slightly (10mL methylene chloride replaced with 50mL isopropyl alcohol 70%, e.g.), the process and resulting calculations remain unaltered.
As a percent weight per unit mass, the active oxygen content of a peroxide species may be determined.

〖AO(%)〗_theoretical=H*16p/m (1)
where
H = % peroxide solution (e.g. 100%)
p = number of peroxide groups in the molecule
m = molar mass of the peroxide molecule
In the case of hydrogen peroxide, p = 1, and m = 34.0147 g/mol. This suggests that a 100% hydrogen peroxide solution contains ~47% active oxygen. This is due to the fact that only one of the oxygen atoms in H2O2 is considered “active.”

ASTM E298 goes on to describe the calculation for determining the experimental active oxygen content in a hydrogen peroxide solution:
〖AO(%)〗_experimental=0.8(A-B)N/W (2)
where
A = mL sodium thiosulfate required to titrate solution to clear endpoint
B = mL sodium thiosulfate required to titrate blank solution (without peroxide) to clear endpoint
N = normality of sodium thiosulfate solution
W = grams of sample used
Eq. (2) gives a percentage of active oxygen. If we want to determine the amount of hydrogen peroxide, simply divide Eq. (2) by Eq. (1). See example below.
Test Samples
Each shipped sample contains ~200mL of a given product.

Process
Utilizing the test method outlined in the next section for all product samples, the following process details the data that EnvirOx would like to obtain from these tests:
Test and record AO and % peroxide for each concentrate.

Dilute each product to create ~1000mL of ready-to-use (RTU) solution. See Table 1 for dilution ratios. Dilute with tap water.
Immediately Test and record AO and % peroxide for each RTU.

Test and record RTU AO daily for two weeks (10 data points per product). Test and record RTU AO once a week for 6 weeks (6 data points per product). Report data to EnvirOx upon completion.

Test Method
Weight out ~0.5g of the product in Erlenmeyer flask – whether concentrated or diluted product. Record mass to 3 significant figures.

Add 50mL isopropyl alcohol.
Add 5mL acetic acid, swirl to mix.

THIS STEP MUST BE PERFORMED BEFORE STEP 4 TO MAKE THE TEST SOLUTION ACIDIC BEFORE ADDING SODIUM IODIDE. FALSE LOW READINGS WILL RESULT OTHERWISE.
Add 5mL sodium iodide solution.
Stir and heat solution to 160°F.
Titrate with sodium thiosulfate solution to clear endpoint. Record amount of titrant required in mL.
Calculate AO and % peroxide in accordance with Eq. (1) and (2).

Example
Weigh out 0.500g of EnvirOx Concentrate 117 in Erlenmeyer flask.
Add 50mL isopropyl alcohol
Add 5mL acetic acid, swirl to mix
Add 5mL sodium iodide solution
Stir/heat mixture to 160°F
Titrate with ~11.6mL sodium thiosulfate to clear endpoint
Perform AO, % H202, ppm calculations
AO(%)=((0.8)(0.1)(11.6-0))/0.500g=1.86%
% H2O2=1.86% 〖[16(1)/34.0147]〗^(-1)=3.95%
3.95% = 39,500ppm
Dilute Concentrate 117 per the label instructions to create ~1000mL
1000 (1/12.8) = 78.125g Concentrate 117
1000 (11.8/12.8) = 921.875g tap water
78.125g Concentrate 117 + 921.875g tap water = ~1000mL RTU (SG~1.01)
Repeat steps 1-8 on RTU in accordance with Process section outlined above.

Results:

Background on Contact Angle Measurements
Residue build up is big part of our value proposition and due to that we really need to develop a testing methodology. Therefore, a need exists to develop a test that looks at residue buildup and long-term streaking with repeated use of the same product.

To address the residue buildup, drop shape analysis is a convenient way to measure contact angles and thereby determine surface energy. Contact angles are an easy-to-visualize and measure manifestation of surface energy, which in turn is a characteristic of chemical bonding. Contact angles, per se, describe the shape of a liquid drop resting on a solid surface.

Figure 1 Contact Angle Description

Contact angles are measured by fitting a mathematical expression to the shape of the drop and then calculating the slope of the tangent to the drop at the liquid-solid-vapor (LSV) interface line.

Figure 1 defines the contact angle, which is nothing more than the angle between a tangent drawn on the drop's surface at the resting or contact point and a tangent to the supporting surface. The important concept is that the shape of the drop reveals information about the chemical bonding nature of the surface. This bonding will determine its wettability and adhesion. The relationship of drop shape to bonding is contact angle's utility.

Water is a good starting place because it is safe and forms a high, easily observed, contact angle on most materials. A simple contact angle measurement with water will give an approximate answer. This is useful because almost all "contaminants" on a surface affect the measured surface energy.

Contaminants will change the contact angle if their surface energy is different from that of the clean surface. Since contact angle is a measure of interfacial energy, which is to say the chemistry of the surface, most contaminants will have a different chemistry and different surface energy.

Metals and semiconductors ("semi-metals") tend to have high surface energies. Metal and semiconductor oxides have medium to high surface energies also. Grease, oils, hydrocarbons and polymers tend to have low surface energies, on the other hand. Therefore, if a clean substrate is a metal or semiconductor, we expect hydrocarbon and polymer contaminants to lower the surface energy. Conversely, if the substrate were pure Teflon, one of the lowest energy solid surfaces available, we would expect most any contaminant to raise the surface energy.

It is important to understand what type of material (surface energy-wise) the substrate is and roughly what to expect from the contaminant.

The Girifalco-Good-Fowkes-Young theory gives us an easy-to-use relationship between surface energy of the solid, surface tension of the test liquid, and the contact angle of the liquid on the surface. Basically, for ordinary surfaces exposed to air surface energy will vary from 73 down to 18. Notice contact angle goes up as surface energy goes down.

Unsatisfied bonds (on the outer edge of a material) constitute surface energy, a potential energy in the sense that another object brought up close might be able to satisfy some of these "dangling" bonds. These bonds are the source of wetting and much of adhesion. Contact angles can be used to estimate the nature and strength of these bonds, mainly because of the lack of a direct-reading meter as in the way one can use a thermometer for temperature or a voltmeter for voltage.

1. Contact angles are measured in degrees. "Low" is below about 20° and "high" is 90° or above. Water on Teflon is about 112°, very high. Low angles mean "wettable."
2. Surface energy and surface tension are measured in dynes/cm (in the old cgs system) or mN/m or mJ/m2 in mks. Fortunately, the numerical values are all the same, so no conversion is required. Water has a surface tension of 72.8 at room temperature. Most solids fall between 15 and 100.
3. If the surface tension of the fluid is below the surface energy of the solid, the fluid will spread rather

than staying in a little droplet.
4. Good adhesives "wet" the surface so they will fill all of the little voids in a real surface and therefore have more bonds in contact.
5. Any contact angle depends on both the solid and the liquid, so you must specify both. Water is a common test fluid. Surface energies have the benefit of theoretically being independent of fluid.

Testing Process
To assess the residue left after cleaning and residue left after multiple cleaning applications, the use of contact angle measurement should demonstrate in the laboratory setting what amount of residue is left behind. Using a First Ten Angstroms FTA1000 Student Goniometer, a small drop of DI water was applied to the glass surface. This would establish a baseline level for the surface energy of the coupons. With the baseline recorded, several scenarios of treating the surface were conducted followed by a "dirty" contact angle measurement to assess the effect on surface activity. Scenarios incorporated were as follows: spray surface and allow to dry, no wiping; spray the surface, wipe with paper towel, allow to dry; spray the paper towel, wipe the surface; spray the surface three times, wipe the surface; spray the surface five times, wipe surface; and spray the paper towel five times then wipe surface. Each of the scenarios was used to try and simulate various cleaning methods.

Results for Glass Surface
Average contact angle measurement for glass coupons was calculated from baseline readings from each coupon used (total of 30 coupons). The average angle was 24.50. During calculations, to normalize results, the difference between the baseline and the "dirty" readings was calculated as a percent change from the initial reading. The greater the percent difference equates to more left on surface, thus lowering surface tension or simpler terms, more residue. Three drop measurements were made for each product and each simulated cleaning process.

For the application of the product to the surface with no wiping, each of the five products lowered the contact angle during the first application of the products. In a majority of the drop readings, no contact angle was measureable (complete wetting of surface) for the five products. EnviOx #117 was found to lower the angle the most followed by product 3, 2 #118 and 1. For the one wipe, product #117 left the least residue followed by product 2, 1, 3 and #118. When applying the spray to towel and then wiping, residue levels were reduced with product #118 producing the least, followed by product 3, 2, 1 and #117. The addition of more sprays onto surface then wiping resulted in an increase in residue left behind. Product #1 had the least followed by #117, #118, 2 and 3. When the sprays increased to five, product #118 left behind the least residue and the other four were about the same as each other. And lastly, when the towel was sprayed directly five times, product 1 had the lowest reside and the other four were about the same as each other.

The first table lists the baseline readings and the dirty readings for each glass coupon and cleaning process. The second contains the calculated percent difference from initial and dirty.

| Process | P 1 | | P2 | | P3 | | #117 | | #118 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Base | Dirty | Base | Dirty | Base | Dirty | Base | Dirty | Base | Dirty |
| 0 Wipes | 24.14 | 8.08 | 23.24 | 2.65 | 24.52 | 2.69 | 24.61 | 1.13 | 18.65 | 5.53 |
| 1 Wipe | 34.68 | 14.52 | 23.14 | 11.34 | 26.34 | 8.53 | 32.13 | 17.10 | 28.97 | 1.38 |
| 1 Spray Wipe | 24.15 | 19.21 | 20.44 | 16.49 | 19.86 | 16.49 | 26.92 | 18.42 | 20.14 | 17.37 |
| 3 Spray Wipe | 21.89 | 15.84 | 22.41 | 14.25 | 17.72 | 9.47 | 21.80 | 15.69 | 22.19 | 15.54 |
| 5 Spray wipe | 19.09 | 14.66 | 22.97 | 16.91 | 18.37 | 14.60 | 20.15 | 14.26 | 18.51 | 18.13 |
| 5 Sprayed Wipe | 33.99 | 25.36 | 32.07 | 19.14 | 31.57 | 20.87 | 30.64 | 18.27 | 29.70 | 19.72 |

Table 2. Percent Difference of Contact Angle Measurements Glass

| Process | P1 %Diff | P2 %Diff | P3 % Diff | 117 % Diff | 118 % Diff |
|---|---|---|---|---|---|
| 0 Wipes | 66.54 | 88.61 | 89.03 | 95.43 | 70.37 |
| 1 Wipe | 58.12 | 50.99 | 67.60 | 46.76 | 95.23 |
| 1 Sprayed Wipe | 20.48 | 19.34 | 18.74 | 31.59 | 13.75 |
| 3 Sprays then Wipe | 27.63 | 36.41 | 46.56 | 28.03 | 30.00 |
| 5 Sprays then Wipe | 23.19 | 26.37 | 20.54 | 29.23 | 2.10 |
| 5 Sprayed Wipes | 25.40 | 40.31 | 33.89 | 40.37 | 33.61 |

Follow Up Testing Results

Stainless steel and plastic surfaces were subjected to the same basic protocol as the glass surfaces. The only difference was that both surfaces showed less change in surface tension and did not need to have all the scenarios followed.

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For stainless steel, three products, P3, #117 and #118 resulted in the surface energy to increase after being wiped as shown by the negative percent difference for the 1 sprayed wipe cleaning process. The P3 product had a similar result after 3 sprays and wipe. Both P1 and P2 had little change in its surface energy with either method of application.

For plastic, P1, P2 and #118 had little change in surface energy after application cleaning process. Product P3 and #117 and a marginal increase after spraying and wiping.

Table 3. Contact Angle Measurements Stainless steel

| Process | P 1 | | P2 | | P3 | | #117 | | #118 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Base | Dirty | Base | Dirty | Base | Dirty | Base | Dirty | Base | Dirty |
| 0 Wipes | 70.74 | 56.10 | 72.79 | 58.16 | 74.54 | 59.55 | 72.53 | 54.82 | 74.20 | 49.56 |
| 1 Wipe | NT | | | | | | | | | |
| 1 Sprayed Wipe | 70.21 | 68.77 | 72.03 | 69.67 | 64.40 | 67.12 | 63.18 | 63.69 | 61.94 | 64.39 |
| 3 Sprays Wipe | 51.72 | 51.16 | 50.19 | 49.76 | 51.83 | 55.08 | 57.40 | 51.14 | 55.53 | 49.13 |
| 5 Sprays wipe | NT | | | | | | | | | |
| 5 Sprayed Wipes | NT | | | | | | | | | |

Table 4. Percent Difference of Contact Angle Measurements Stainless steel

| Process | P1 %Diff | P2 %Diff | P3 % Diff | 117 % Diff | 118 % Diff |
|---|---|---|---|---|---|
| 0 Wipes | 20.62 | 20.09 | 20.1 | 24.42 | 33.2 |
| 1 Wipe | NT | | | | |
| 1 Sprayed Wipe | 2.05 | 3.27 | -4.23 | -0.8 | -3.97 |
| 3 Sprays then Wipe | 1.09 | 0.85 | -6.28 | 10.9 | 11.52 |
| 5 Sprays then Wipe | NT | | | | |
| 5 Sprayed Wipes | NT | | | | |

Table 5. Contact Angle Measurements Plastic

| Process | P 1 | | P2 | | P3 | | #117 | | #118 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Base | Dirty | Base | Dirty | Base | Dirty | Base | Dirty | Base | Dirty |
| 0 Wipes | 58.21 | 44.2 | 50.56 | 41.61 | 62.89 | 50.19 | 54.6 | 47.38 | 53 | 49.73 |
| 1 Wipe | 54.58 | 54.52 | 53.63 | 53.24 | 63.04 | 58.56 | 56.06 | 49.4 | 62.15 | 60.75 |
| 1 Sprayed Wipe | 57.58 | 57.28 | 56.90 | 54.53 | 55.15 | 51.41 | 54.19 | 49.48 | 49.93 | 46.52 |
| 3 Sprays then Wipe | NT | | | | | | | | | |
| 5 Sprays then wipe | NT | | | | | | | | | |
| 5 Sprayed Wipes | NT | | | | | | | | | |

Table 6. Percent Difference of Contact Angle Measurements Plastic

| Process | P1 %Diff | P2 %Diff | P3 % Diff | 117 % Diff | 118 % Diff |
|---|---|---|---|---|---|
| 0 Wipes | 23.98 | 17.71 | 20.20 | 13.22 | 6.18 |
| 1 Wipe | 0.10 | 0.73 | 7.11 | 11.89 | 2.26 |
| 1 Sprayed Wipe | 0.54 | 4.17 | 6.79 | 8.70 | 6.82 |

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| 3 Sprays then Wipe | NT | | | | |
| 5 Sprays then Wipe | NT | | | | |
| 5 Sprayed Wipes | NT | | | | |

Summary:

Conclusion:

Conclusions

It is apparent from the basic contact angle measurements that each cleaning product will leave behind residue if left on the surface to dry. Wiping the surface helps to reduce the residue levels. Spraying the wipe and then wiping surface should leave the least amount residue behind on the surface. There were no clear trends as to which supplied cleaning product produced the least amount of residue. However, Product 1 and EnvirOx #118 more consistently left lower levels of residue.