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A Study of the Differences in Means in Antioxidants

Purpose of Study

Antioxidants are used in many applications to increase the useful life of a substance or to prevent degradation or oxidation. In the lubricant and fuel market antioxidants are added to extend the life of the lube or fuel. Antioxidants can also be added to polymers to prevent degradation from sun exposure and to increase the useful life of the product.

Oxidation can be generated by heat, metals, and other impurities. When oxidation is initiated the bond between to elements is broken and a free radical is formed. During propagation phase a free radical will react with other stable molecules to from new free radicals. These new free radicals go on to generate even more free radicals as the propagation step continues to repeat itself again and again. When termination occurs two radicals react with each other to form a stable non-radical new molecule. Antioxidants promote the termination step once initiation and propagation are in full effect. Antioxidants sacrifice some of their own electrons so they can safely interact with the free radicals and promote termination through bonding. Below you will find a reaction of the steps that occur during oxidation.

initiation

$$\overrightarrow{A}$$
 \overrightarrow{B} $\xrightarrow{\text{(heat or light)}}$ \overrightarrow{A} $+$ $\overset{\bullet}{\cdot}$ \overrightarrow{B}

propagation

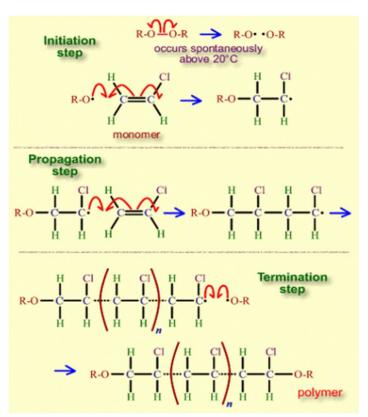
$$A \xrightarrow{C} C \xrightarrow{D} \longrightarrow A - C + \cdot D$$

$$D \xrightarrow{F} D - E + \cdot F \longrightarrow \text{etc.}$$

termination

$$F \cdot + \cdot G \longrightarrow F - G$$

PVC manufacturers have two possible options for adding an antioxidant. It can be added as a primary antioxidant which is added to the reactor before polymerization or as a secondary antioxidant which is added to the reactor after polymerization. The PVC plant I worked for used a primary antioxidant (AO). Below you will see how the process for manufacturing PVC.



The PVC reaction steps look very similar to the oxidation reaction described above for oxidation. PVC utilizes the same steps to take a vinyl chloride monomer starting material and grow the chain to polymerize it into polyvinyl chloride (PVC).

I was asked to review many possible antioxidants used for PVC manufacture in the pilot plant to see if there was any benefit from using one stabilizer over the other. I designed an experiment to test fifteen different AO's at various treat rates.

The experiment identified one promising BASF antioxidant that if added post polymerization could speed up the batch reactor time by 1.5

minutes or reduce batch cycle times by \approx 4%. In the chart below you will find the treat rates for each antioxidant along with the cost of each antioxidant. We ran a plant wide trial to test the new AO and compare it to the control to determine if the new antioxidant was truly different in reaction time when compared to the original AO or our control.

Antioxidant	Treat Rate	Antioxidant Type	Cost per Annum
Control	80 ppm	Primary	\$90,000
New	140 ppm	Secondary	\$240,000

The following hypothesis will be used to test at the plant wide level (which is far more costly than testing and experimenting in the pilot plant).

 $H_0: \mu_{control} = \mu_{new}$ $H_A: \mu_{control} \neq \mu_{new}$

 $H_0: \mu_{control} - \mu_{new} = 0$

 $H_A: \mu_{control} - \mu_{new} \neq 0$

 H_{o} : The mean batch time of the control or original antioxidant system is equal to the mean batch time of the new antioxidant system.

 H_A : The mean batch time of the control or original antioxidant system is not equal to the mean batch time of the new antioxidant system.

Analysis Plans

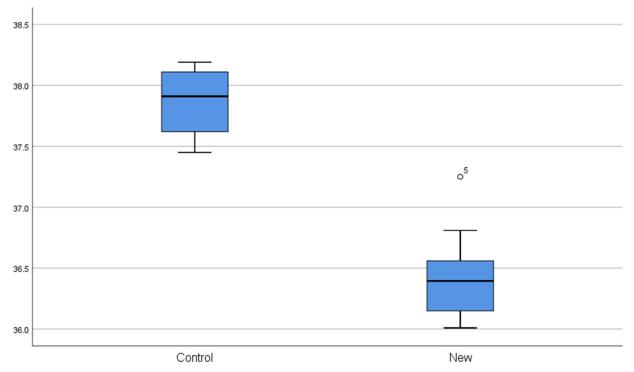
<u>Descriptive Statistics</u> – The descriptive statistics provide a basic summary of the data. It can be used to compare data sets and look for patterns. The descriptive statistics is usually a great place to start when analyzing datasets.

<u>Boxplots</u> – The boxplots provide a great graphical representation of the data side by side. The boxplots show where the median is located. We can also identify any outliers by looking at the box plot.

<u>t-test</u> – When comparing the difference between two means the z-test is used when the standard deviation is known, and the variables are normal (or the sample size is 30 or greater for each sample). The t-test is used when the standard deviation is not known and the sample size for one or both samples is less than 30. For this data set and experiment we will use the t-test to examine if the sample means are equal.

Descriptive Statistics

At this point I partnered with a senior engineer, and we moved our experiment to a plant trial. We chose the newest reactor with the most automation to test AO-2 or the new antioxidant. This reactor that was purchased and installed within the last 5 years provides the most automation, so it is the most reliable reactor for testing. We conducted 20 experiments for the control and 20 experiments for the new antioxidant.



Descriptive Statistics					
	Ν	Minimum	Maximum	Mean	Std. Deviation
Control	20	37.45	38.19	37.8555	.26265
New	20	36.01	37.25	36.4030	.30603
Valid N (listwise)	20				

After running the plant wide trial you can see from the boxplot and the data that there is a difference in time between the average minutes per batch with the control or original anitoxidant and the average time in minutes of the new antioxidant. We did have one sample data point in the new test batch that is an outlier. I asked the senior engineer if we should remove this data point from our data set. His opinion was that we should check the t-test first, and if it passes then there is no reason to remove this data point. From the t-test statistics below you will find the control and the new antioxidant are different. (As a side note in the plant we pulled our "trusty" calculators to perfom this calculation. We crossed checked our results with one another). This confirms that the two antioxidnats tested in this plant trial are indeed different from each other, and the difference of 87 seconds in decreased batch time speed from the new antioxidant is truly different from the control antioxidant batch speed time. Even though we get the same p-value for unequal and equal variances, we should have used the pooled method. From Hartley's test for the equality of variances you will see that the variance for these two variables are considered equal from Lavene's test.

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Control	New
37.68	36.38
37.58	36.15
38.11	36.77
38.19	36.19
38.17	37.25
37.98	36.01
37.56	36.08
37.45	36.25
38.11	36.15
37.51	36.18
38.15	36.58
37.66	36.13
37.48	36.54
37.99	36.81
37.68	36.52
38.01	36.5
38.14	36.58
38.07	36.45
37.75	36.13
37.84	36.41

From the descriptive statistics, you will find when comparing the original or control antioxidant to the new antioxidant the average time went from 37. 86 minutes to 36.41 minutes. This results in a difference of 1.45 minutes per batch. When you employ this chemistry plant wide across all reactors you will see that this 1.45-minute (or 87 seconds) reduction in batch time could potentially produce an additional 2 million pounds of resin. In 2013 the cost per pound of resin was approximately \$0.50 per pound. Therefore, utilizing this methodology could generate an addition 1 million in revenue. This is only one manufacturing plant. If this technology we utilized globally, the increased output would increase respectively with each plant. However, I would most certainly test each plant independently to confirm the results are similar before making any changes to the process.

Summary T-Test

Summary Data

	N	Mean	Std. Deviation	Std. Error Mean
Control	20.000	37.856	.263	.059
New	20.000	36.403	.306	.068

Independent Samples Test					
	Mean Difference	Std. Error Difference	t	df	Sig. (2-tailed)
Equal variances assumed	1.453	.090	16.107	38.000	.000
Equal variances not assumed	1.453	.090	16.107	37.145	.000

95.0% Confidence Intervals for Difference

	Lower Limit	Upper Limit
Asymptotic (equal variance)	1.276	1.629
Asymptotic (unequal variance)	1.276	1.629
Exact (equal variance)	1.270	1.635
Exact (unequal variance)	1.270	1.635

Results and Conclusions

In conclusion, we accepted the alternative hypothesis that the mean average time per batch is truly different than the control. We found that by switching from a primary antioxidant, which slows down the batch cycle time (by reacting with some of the catalyst), to a secondary antioxidant, which is added after polymerization, we were able to speed up the batch cycle time by 90 seconds or 1.5 minutes. This 90 second difference in batch cycle time is confirmed to be a real difference from the student's t-test. Changing from a primary antioxidnat to a secondary antioxidant would cost an additional \$150,000 per year, but it would generate approximately an additional 2 million pounds of PVC resin or roughly an additional 1 million in revenue if the manufacturing plant is operating at maximum capacity.

When I was hired on to work for this PVC manufacturer the economy was in a recession and the plant was not at maximum production capacity. When the manufacturing plant is not at maximum output it makes sense to choose the more cost effective stabilizer even if it results in a slower batch speed. When I tested this antioxidant a few years later the manufacturing plant was sold out of PVC resin. When the production plants are producing at maximum capacity it

makes sense to shift gears and speed up the process time to create even more plant output. This would create more revenue and satify even more customer orders.

Another point that can be made with this data set is the outlier. This outlier is a gentle reminder of how even as the plant managers spend lots of money to upgrade to highly automated reactors and hire the brightest engineers to run the plants, the process still needs to be correctly handled at the operations level to achieve the desired results. The operators physically have their hands on the process. The operations team has just as much control over the process and the quality of the end product as the managerial engineering team does.