

Effects of Gasoline and Ethanol Fuel Corrosion Inhibitors on Powertrain Intake Valve Deposits

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ABSTRACT

Corrosion inhibitors (CIs) have been used for years to protect the supply and distribution hardware used for transportation of fuel from refineries and to buffer the potential organic acids present in an ethanol blended fuel to enhance storage stability. The impact of these inhibitors on spark-ignition engine fuel systems, specifically intake valve deposits, is known and presented in open literature. However, the relationship of the corrosion inhibitors to the powertrain intake valve deposit performance is not understood. This paper has two purposes: to present and discuss a second market place survey of corrosion inhibitors and how they vary in concentration in the final blended fuel, specifically E85 (Ethanol Fuel Blends); and, to show how the variation in the concentrations of the components of the CIs impacts the operation and performance of vehicles, specifically, the effects on intake valve deposit formation. Commercially available corrosion inhibitor packages for both gasoline and ethanol blended fuels, specifically E85 fuels (Ethanol Fuel Blends), were studied for their chemical compositions, and their impact on valves for a naturally aspirated port fuel injection (PFI) engine. Gas chromatography data of E85 blended fuels (Ethanol Fuel Blends) with CIs will be shown and discussed. The PFI engine dynamometer tests were performed in a designed fashion to understand repeatability in the data. This is important due to the wide range in corrosion inhibitor concentration that has been discovered in the market data. Chemical analysis data of the fuels with CIs will be used to explain the intake valve deposit results. Further method developments are ongoing to study the fatty acid portion of the corrosion inhibitor package and its possible contribution to the intake valve deposits.

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INTRODUCTION

Legislative and economic forces require automobile Original Equipment Manufacturers (OEMs) to find every possible method to improve the performance and emissions of their products. This is primarily due to the need to meet the Energy Independence and Security Act of 2007 requiring OEMs to meet a 35.5 MPG CAFÉ by 2016, and as of October 2012, the "2017 and Later Model Year Light-Duty Vehicle Greenhouse Gas Emissions and Corporate Average Fuel Economy Standards, Final Rule"(1,2,3). In addition, OEMs want to make sure that the vehicles maintain optimal performance over the life of the product. One area that has been of particular interest is the impact of the fuel chemistry on the fuel delivery system.

In 2004, a gasoline detergency program called TOP TIER Detergent Gasoline was created by several automotive sponsors to enhance engine cleanliness. This program promotes marketplace gasoline detergent additive concentrations higher than the EPA's lowest allowable concentration, as mandated by the Federal Clean Air Act of

1996. By passing a rigorous series of engine deposit and injector performance tests, the candidate fuel is given a TOP TIER rating that confirms it will help maintain a engine's optimal performance (4).

The precise control of a vehicle's air and fuel delivery systems is critical for the ideal performance of an internal combustion engine. Disruptions in the ideal fuel and air mixture ratio can lead to power, emissions, and driveability problems. As part of the engine's induction system, the intake valves are the components responsible for the delivery of the fuel and air mixture between the intake manifold and the interior of the combustion chamber. If there are deposits on the intake valves, this can compromise the ideal filling into the cylinder and spray pattern of the fuel for efficient combustion of the fuel.

For many years, fuel related intake valve deposits have been a concern and therefore there have been many studies with regard to the mechanism of deposit formation; the influences of fuels, lubricating oil and engine characteristics; and, the impacts they have on power, emissions and fuel

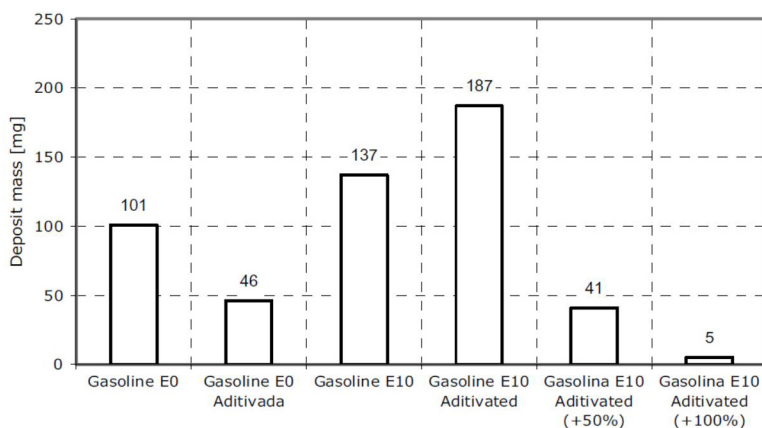


Figure 1. Ethanol Influence on Intake Valve Deposits (9)

(5,6,7,8). Some of those studies are presented in the following paragraphs.

Shiblom and Schoonveld performed tests of 5000 miles on BMW 318i vehicles, which had port fuel injection (PFI) injectors, using gasoline and ethanol blended fuels to observe their influence on intake valve deposit (IVD) formation. They found the use of ethanol increased the IVD formation when the ethanol was added to unadditized gasoline as well as splash blended on top of pre-additized gasoline. In addition, the deposits weights observed from the tests with the pre-additized gasoline mixed with ethanol were higher than those from unadditized gasoline and gasoline mixed with ethanol (9). This is shown in Figure 1, recreated in the work by Mello and Sá (10), referencing the work of Shiblom and Schoonveld (9). In the figure, the IVD is reported as the average of the IVD mg per cylinder. In the figure, labeled as “Aditivada” and “Aditivada”, the additive that was used meets the Criterion 1 of the BMW standard of intake valve deposit test for 5,000 miles, depositing up to 50 milligrams maximum. For the bar labeled as “Aditivada (+50%)” indicates that the additive is added in a concentration 50% higher than “Aditivada”; for the bar labeled as “Aditivada (+100%)” indicates that the additive is added in a concentration 100% higher than “Aditivada”. To solve the deposit increase, the additive dose was increased and tested, showing improved results. In a similar study, Tupa and Koehler observed the same tendency when using methanol and gasoline mixtures (11). As there was no analysis of the alcohols provided it is unclear to the quality of the ethanol and methanol tested or if they were additized with corrosion inhibitors as is today's ethanol industry practice.

Another more recent study by DuMont and colleagues also focused on controlling the induction system deposits with an engine operating on 85% ethanol blends (12). In this study, a series of 5000 mile chassis dynamometer intake valve deposits and performance tests were conducted on model year 2006 General Motors Chevrolet Impala Flexible Fuel Vehicles. The powertrain was a 3.5L, naturally aspirated, V6 sequential fuel injection (SFI) engine with E85

capability. The vehicles were run on conventional gasoline and on E85 to show the deposit forming tendencies of both fuels. In their study, the E85 test fuels were found to generate significantly higher levels of IVD than the conventional gasoline. The study comprised the use of two different sources of ethanol. The two ethanols had different amounts of denaturant, with Ethanol B having 2 wt % less than Ethanol A, and Ethanol A had 116 ppm of CI, while Ethanol B had only 3 ppm. They hypothesized this increase in IVD was due to a corrosion inhibitor and sulfates that were present in one of the ethanols tested, and made further studies on these. To the Ethanol B, two different types of CIs were added at the same treat rate as Ethanol A had, “X”- a buffered CI and “Y”- an unbuffered CI. The results of that study are shown in Figure 2 (12). It is clear that the CI “X” gave the same level of IVD as Ethanol A, while the unbuffered “Y” CI was IVD neutral. Finally, as part of this work, deposit control additives (DCA) were used to show that the IVD from the E85 fuels could be minimized. In particular, the polyisobutylene amine- and the polyether amine- based control additives showed to be effective.

From the petroleum refinery and through the petroleum supply pipelines and trucks that deliver gasoline and ethanol to the supply terminals, internal corrosion of the fuel distribution system metallurgy is a serious problem; safety, environmental contamination, contamination of the fuel products and the vast expense of the infrastructure (13,14,15,16). CIs are an important safeguard against many of these concerns and operate by passivating the metal surfaces and in some cases buffer any organic acids that may form. Increased use of fuel alcohols has increased the need for effective corrosion inhibitors. For many years, oligimerized fatty acid corrosion inhibitors, commonly known as a dimer acids have been used in the transportation of conventional gasoline (17). In recent years, with the increase of the use of ethanol, a new series of corrosion inhibitors have been created for use specifically with alcohol fuels. Some of these can be found on the Renewable Fuel Association website (18). These CIs are generally made up of

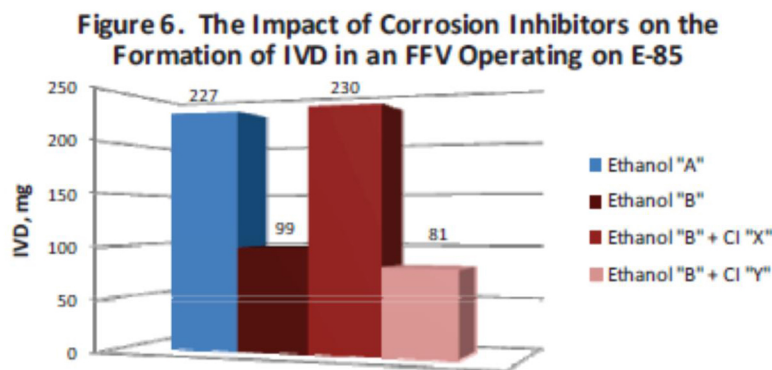


Figure 2. The impact of Corrosion Inhibitors on the Formation of IVD in an FFV Operating on E85 (12)

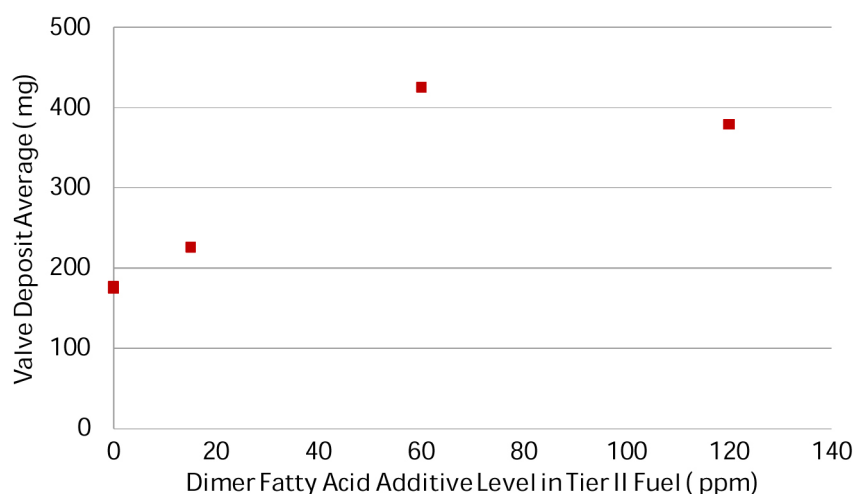


Figure 3. Intake Valve Deposits (mg) vs. Dimer Fatty Acid Concentration (ppm) (19)

a combination of fatty acids an amine, and a solvent carrier, in various combinations depending on the manufacturer. In the fuel distribution system and final blending of the ethanol into gasoline, it is possible that both of the fuels, gasoline and ethanol, are treated with the corrosion inhibitor separately and potentially together. Petroleum refineries are adding the CIs to the gasoline before it is placed into the pipelines, and the ethanol producers adding the CIs to the ethanol. As the cumulative concentration of the CI increases, the result of this may potentially be high levels of IVDs.

The authors have completed previous work with increasing concentration of a dimer fatty acid component of the CI package (19). Shown in Figure 3, the results of the study with Tier II gasoline with increasingly added dimer fatty acid concentrations showed that as the fatty acid concentration increased, the amount of IVD increased.

CI additive concentration in the market fuel supply is not well known and understood. The purpose of the following study has two parts: 1) to generate chemistry data from E85 fuel surveys to understand if there is "over" addition in the marketplace and to what extent, and 2) to show the

magnitude of the impact of the marketplace representative CI treat rates on IVDs and engine performance.

Common Engine Testing Methodologies for Intake Valve Deposits Measurements

The BMW IVD test (ASTM D5500) was developed at Southwest Research Institute© in the late 1980s and uses a 4 cylinder 1985 BMW vehicle, driven over the road. The cycle for the test is repeated to accumulate a total of 10,000 miles per test. After the test is complete, the intake valves are removed from the engine, weighed, and visually assigned a merit rating. If the valves produce an average of less than 100 mg, it receives the unlimited mileage certification (20).

The FORD 2.3L IVD test (ASTM D6201) was developed under the direction of the Coordinating Research Council in the 1990s. The test is performed in a controlled environment using an engine dynamometer. The IVD engine cycle lasts 13 minutes, and is repeated for 100 hours. Once completed, the engine is disassembled, valves are weighed, and a pass or fail is given based on the average weight of 130 mgs over all 4

Table 1. North American E85 (Ethanol Fuel Blends) Sample Trends 2009-2012 vs. ASTM D5798-11 Specification (23)

Test Parameter	2009 % Failed	2012 % Failed	Comments
RVP (psi)	88%	30%	Class 2 has the most out of spec.
pHe	12%	5%	Does NOT trend with corrosion inhibitor content.
Water (wt%)	0%	0%	Does trend with conductivity.

Table 2. North American E85 (Ethanol Fuel Blends) Sample Trends 2009-2012 vs. Other Properties

Test Parameter	2009	2012	Comments
Sodium (ppm)	12% contained	100% contained	GM recommendation is 0 ppm sodium.
Corrosion Inhibitor Treat Rate average (ppm amine)	30.17	6.95	Does NOT trend with washed gum content.
Corrosion Inhibitor Max – Min (ppm amine)	63.92 – 2.04	12.61 - 1.74	Low values may indicate a different amine type used or the actual low concentration.

valves, which was deemed equivalent to the 100 mg from the BMW test (21).

MARKET PLACE SURVEY DATA AND EXPERIMENTAL TESTING

Marketplace Survey Data

Cummings and Chapman conducted surveys in 2009 and 2012 to focus on trends related to critical chemical properties in E85 (Ethanol Fuel Blends) fuel that can affect the fuel system metallic components and also the engine performance (22). In Table 1 below, a summary chart of trends for chemical properties that failed the ASTM D5798-11 specification for the E85 (Ethanol Fuel Blends) blended fuels in each year of the survey (23). The survey consisted of the same set of 17 fuel stations across the US, with the addition of 3 fuel stations in Michigan in 2012. All of the fuel samples were collected and analyzed during the summer months, and then any contamination of the fuels due to winter road salts washing into the fuel storage facilities has been eliminated from this data set.

Table 2 shows properties that are not currently specified by ASTM D5798-11, but that the authors hypothesize have an impact on the engine and vehicle performance, including the change in corrosion inhibitor found in the fuel.

The sodium content of the fuel is of concern as that can be corrosive to the fuel system and a source for forming carboxylate salts (24). There are various sources of sodium from the point at which the fuel is refined to the delivery into a customer's personal vehicle at a refueling station. These

sources include the sodium hydroxide caustic and sodium chloride salt from refineries, sodium sulfate contamination from ethanol scrubber washing, and the road salts that are washed into storage tanks at refueling stations. Sodium sulfate contamination from ethanol production is believed to be from the sodium bisulfite that is used to clean down the scrubbers in the ethanol production process (25). If an overtreatment of sodium bisulfite is used it can react with any acetal aldehydes to form ethanol and sulfate which are soluble in the scrubber water solution and can eventually get sent to the distillation column (25). With any water left in the ethanol from the distillation process, over time the sulfite could oxidize into sulfate (25). This can lead to the high ion content of the ethanol that gets blended into fuel thus causing a high conductivity value, a potentially high pHe value, and a challenge for the corrosion inhibitor if the sodium cation forms carboxylate salts which are known to aid in the development of deposits (26).

The corrosion inhibitor amine type and concentration is important as amines are soluble in blends of ethanol and gasoline but can be overtreated and create a precipitate (17). The amine is only 20-40% of an ethanol corrosion inhibitor package but is a compound that can create a plating (chelating) effect on a metallic surface if the concentration is too high and drastic temperature changes are experienced (17).

The fatty acid is 40-60% of a corrosion inhibitor package and can be in the form of a monomer, dimer, or trimer acid (17). The remaining 20-40% of a corrosion inhibitor package is the carrier solvent used to keep the other components in

solution and to blend well into the hydrocarbon base of the gasoline and polar OH base of the ethanol (17). The fatty acid types have molecular weight distributions that can be well controlled but the trimer acid is the most difficult to control (17). It is, however, the most effective and thus the most expensive corrosion inhibitor package (17). The monomer is less effective, and the dimer is the most popular because of performance and the ability to control corrosion at a reasonable price (17). The key for ethanol blended fuels is to find a concentration that will protect the distribution system, enhance the fuel storage stability, minimize risk to the engine performance, and optimize cost (17).

Below is the table showing the complete results for the 2012 E85 (Ethanol Fuel Blends) market place survey, [Table 3](#). The corrosion inhibitor column is broken down into the two most common types of amines used in corrosion inhibitor packages today (18). In the columns with the Corrosion Inhibitor Amine (ppm), where there is an x listed, this means that the material was not found. The variability in treat rates in ppm (part per million) indicates that some fuel blenders are using one type versus another and the concentrations vary widely from <2 ppm to almost 13 ppm. This is an improvement from the 2009 E85 market place survey samples where the range was 30 ppm to 0.5 ppm. It should be noted that if the Type 2 column value is low, this may be indicative of either a low treat rate or the blender uses a different type of amine not common in the market place. Cells that are highlighted in red indicate that the value failed to meet the required ASTM D5798-11 fuel specification (23). The required ethanol content is between 51-83%, so anything over 83% would be out of specification. The RVP requirement depends on the date and location where the fuel is sold which indicates which "Class" it is sold under, and so there were several of the samples that had a low RVP for their specific Class.

Experimental

The IVD testing for this study was completed on an engine dynamometer set up. The engine used in the study is GM's LE9 (2.4L) engine, the engine used on the 2009 Chevrolet HHR, capable of using E85 fuels. This is a naturally aspirated port fuel injected (PFI) engine. [Table 4](#) shows the details of the engine.

Because IVD is the difference in valve weight before and after the test, the engine valves were weighted, in accordance with the procedure from ASTM 5500. An engine test cycle with a long soak period was developed because previous work suggested that this will generate a significant amount of IVDs. This cycle was completed over a 3 week period which ends when the 150 total test cycles are achieved. After the test was completed, the engine was disassembled and the valves were weighed, similar to the ASTM D5500 test procedure. The deposit weights were calculated and summed for the two intake valves in each of the four cylinders.

The purpose of this test was to focus on the intake valve deposits and not the injector deposits. However, the test

procedure collects data with regard to the injector functioning during the test, and the data can be reviewed later as the IVD analysis suggests. During the test, the air to fuel ratio is collected to determine if injector fouling is occurring, with air to fuel ratios greater than the stoichiometric for the particular fuel being used is indicative of plugging injectors. In addition, the Engine Control Module (ECM) variable for fuel adaptation was monitored throughout the test to show any shift in the performance. Fuel injectors for each test were photographed for future inspection. All fuel injectors are saved for further analysis if desired.

The test fuel used for this study was a refinery based 91 Octane fuel with 0% ethanol that was provided without detergents and corrosion inhibitors, at an RVP of 7.6 psi. The fuel was prepared with ethanol (an Ed98) that did not contain corrosion inhibitors in two different types of blends, as an E72 and as an E15. The E72 was used to represent a high ethanol content fuel level, and the E15 was used to represent a low ethanol content fuel. Typical fuel properties for the 91 Octane fuel are shown in [Table 5](#).

The test plan for the two fuels types was constructed to provide an understanding and guidance of the impact of the components of the corrosion inhibitor package on the IVDs for the engine. CIs designed for ethanol use are typically made of three components, a fatty acid, an amine, and a solvent carrier. The test plan consisted of preparing the components separately, and blending them into the fuels that were also blended in the specific ethanol concentrations. When an additive concentration is mentioned, i.e. 15 ppm dimer fatty acid, this is referring to the active amount of the substance that is blended into the carrier. Each portion of a typical ethanol corrosion inhibitor package were prepared separately into the carrier, and then blended into the fuel barrels. So, a particular test running an acid and an amine with have two bottles prepared, one with the acid in the carrier and the other with the amine in the carrier. Dimer fatty acid was the main acid used because it is most widely used in the industry. For comparison, a monomer fatty acid was used for some testing. The amine used was dimethylcyclohexylamine (DMCHA). The components were blended to normal and over dosed treat rates, to determine the impact of increasing the additive concentration dosing. The concentration curves that were created are presented in tabular form in [Table 6](#). During this IVD study, the CIs used were single component blended with a solvent carrier, i.e. non-buffered. Solutions of the appropriate concentrations of the CIs were bottled so that they could be blended with 50 gallon drums of the fuel.

Because of the significant number of tests that needed to be run, three LE9 2.4L engines were set up to run all the tests for the E72 fuels, and the same dyno was used to run the E15 fuels. In the text, the engine dyno stands are referred to as STD, or Stand or engine dyno, and sometimes by the particular engine dyno stand number. All E72 tests were run on engine dyno stands 4, 7, and 8. All of the E15 tests were run on engine dyno stand 3. To maintain consistency in the

Table 3. North American E85 (Ethanol Fuel Blends) Sample Analysis Data (2012 samples)

Collection Date	State	Location	EtOH	MeOH	Water	RVP	Unwashed Gum	Washed Gum	Sp. Gravity	Conductivity	pHe	Chlorides	Sulfate	Sodium	Total Ions	Sulfur	Corrosion Inhibitor	Total Amine
			vol%	vol %	mass %	psi	mg/100mL	mg/100mL	g/cm3	uS/cm		ppm	ppm	ppm	ppm	ppm	Type 1 DMEA Type 2 DMCHA	ppm
5/22/2012	MI	Bay City	80.66	0.06	0.80	6.28	2.6	0.2	0.7815	0.6	7.43	0.05	0.00	6.10	6.15	5.94	x	11.26
5/23/2012	IL	East Peoria	83.89	0.03	0.90	5.66	3.3	0.3	0.7849	0.9	7.66	0.04	0.03	6.70	6.77	3.89	x	12.61
5/23/2012	IA	Oskaloosa	70.94	0.01	0.70	8.12	3.5	0.3	0.7749	0.5	7.38	0.08	0.12	5.60	5.80	8.71	x	7.13
5/24/2012	GA	Hinesville	85.21	0.04	0.90	5.48	2.1	0.5	0.7851	1.0	7.37	0.13	0.00	7.60	7.73	5.13	x	8.65
5/23/2012	TX	Houston	86.51	0.07	0.60	4.51	1.7	0.4	0.7847	0.5	5.34	0.17	0.13	5.60	5.90	4.52	x	2.05
5/23/2012	GA	Vienna	81.01	0.06	0.90	6.09	3.0	0.6	0.7820	0.8	7.25	0.08	0.00	6.00	6.08	5.85	x	10.63
5/25/2012	CO	Denver	73.86	0.03	0.60	9.05	4.3	0.3	0.7596	1.0	7.23	0.22	0.08	5.90	6.20	3.79	x	10.97
5/27/2012	KY	Simpsonville	71.46	nd	0.80	7.69	5.3	0.2	0.7734	0.6	7.10	0.16	0.00	6.30	6.46	4.98	7.59	2.53
5/27/2012	IN	Jeffersonville	83.36	0.06	1.00	8.33	0.7	0.2	0.7720	0.6	7.25	0.18	0.00	6.90	7.08	14.02	8.48	1.76
5/25/2012	MN	Marshall	77.55	0.02	0.70	10.60	1.2	0.4	0.7622	0.7	7.16	0.02	0.00	5.40	5.42	9.58	10.19	1.74
5/27/2012	AL	Birmingham	84.89	0.04	0.90	5.56	2.3	0.3	0.7851	1.1	7.32	0.15	0.46	6.40	7.01	5.06	x	10.34
5/23/2012	NE	Aurora	46.51	nd	0.30	9.20	7.8	0.4	0.7608	0.3	6.56	0.05	0.00	6.30	6.35	15.09	x	4.85
5/26/2012	FL	Miami	82.17	nd	0.60	5.79	6.5	0.9	0.7806	1.2	6.54	0.19	0.25	3.6	4.04	6.12	x	4.63
5/24/2012	SD	Rapid City	84.52	0.01	0.80	5.50	4.1	0.8	0.7831	0.7	7.50	0.03	0.00	5.1	5.13	4.4	x	9.93
5/27/2012	NY	Fulton	71.84	0.04	0.70	7.08	5.4	0.8	0.7752	0.5	7.22	0.09	0.00	3	3.09	9.24	7.36	4.13
5/24/2012	NV	Minden	84.04	nd	1.00	5.03	3.4	0.2	0.7857	1.0	7.22	0.17	0.36	4.7	5.23	2.13	7.13	5.76
5/24/2012	IL	Chicago	76.12	0.03	0.80	7.31	2.5	0	0.7752	0.5	7.39	0.02	0.00	3.5	3.52	2.38	x	8.81
7/26/2012	MI	Wixom	82.85	0.10	0.92	7.88	1.0	0.9	0.7759	1.4	7.14	0.13	0.00	10.96	11.09	2.59	x	6.33
7/26/2012	MI	Brighton	82.19	0.06	0.91	6.02	2.6	1.3	0.7828	4.4	8.19	0.28	0.30	10.25	10.83	4.36	x	8.50
7/26/2012	MI	Warren	82.31	0.03	0.93	5.79	1.9	1.1	0.7831	2.8	8.16	0.23	1.33	5.21	6.77	9.62	x	7.70