Determining Brake Fluid Quality By Refractometer

A European Study of New and "In-Service" Fluids

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Brake Fluid Quality and Brake Performance

The condition of brake fluid is important to automotive safety, reliability and brake system longevity. Brake fluid absorbs moisture over time. Increasing moisture levels in the brake fluid lower the boiling point, increase viscosity and cause corrosion of system components. Brake fluid with high moisture content can boil when extreme braking is required or a pad sticks. The effect of boiling is the same as when there is air in the system. The pedal sinks to the floor and stopping power is greatly reduced. The increased viscosity of brake fluid with high water content can affect both standard and ABS systems. In cold climates viscous fluid is no longer able to flow freely through the brake lines and fittings. There is increasing awareness among service technicians that water in brake fluid causes corrosion to system components including expensive ABS controllers.

The following is taken from the Society of Automotive Engineers Recommended Practice J1707 "Service Maintenance of SAE J1703 Brake Fluids in Motor Vehicle Brake Systems"

> "3.3.3 Water Contamination - J1703 motor vehicle brake fluids are hygroscopic and absorb moisture when exposed to the atmosphere and in service. Water contamination from any source including mechanical or accidental additions of free water, will appreciably lower the original boiling point of the brake fluid and increase its viscosity at low ambient temperatures. Water contamination may cause corrosion of brake cylinder bores and pistons, and may seriously affect the braking efficiency and safety of the brake actuating system."

Normally brake fluid absorbs 1% to 2% of its weight in water per year. The actual amount of water depends on the condition of the system components, most importantly the hoses. It also depends on the type of brake fluid, humidity and driving conditions. Many motor vehicle manufacturers recommend changing fluid at regular intervals, generally every two years.

This study demonstrates that a large percentage of vehicles have too much water in their brake fluid. The 83 vehicles tested at a TUV Inspection Center in Germany show that even with regular fluid changes being recommended by European automobile manufacturers, high water content is a major problem in the general population of vehicles. Either this recommended service is not being followed or water is entering the system much faster than previously thought.

This work also shows that refractive index is an excellent indicator of the boiling point and water content of the brake fluid from "In Service" vehicles. Refractometers offer many advantages over other types of brake fluid testers. There is no need to remove large samples of fluid for boiling point analysis. A few drops of fluid from the wheel cylinders may even be analyzed. Alternately, there is no need to put a hot probe in the brake fluid reservoir. Boiling older fluid may form precipitates which could plug fluid lines or passageways.

Purpose of the Leica Brake Fluid Study

The purpose of the study is to determine if refractive index can be used as an indicator of brake fluid quality. This study compares the Boil Point, Karl Fischer Water Content and Refractive Index. Samples studied include new European DOT 4 brake fluids with and without water added. Also included are results of a real world sampling of motor vehicles at a TUV test center in Cologne, Germany.

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Leica uses the definitions of brake fluids described by The Society of Automotive Engineers (SAE). To be a valid Brake Fluid it must meet the requirements of SAE Standard 1704 (DOT 4 Type Brake Fluids). The wet and dry DOT 4 boil points specified in the standard are:

> Dry Boil Point: 230°C Standard, 260°C Super
> Wet Boil Point: 155°C Standard, 180°C Super (approx 3.7% Water)

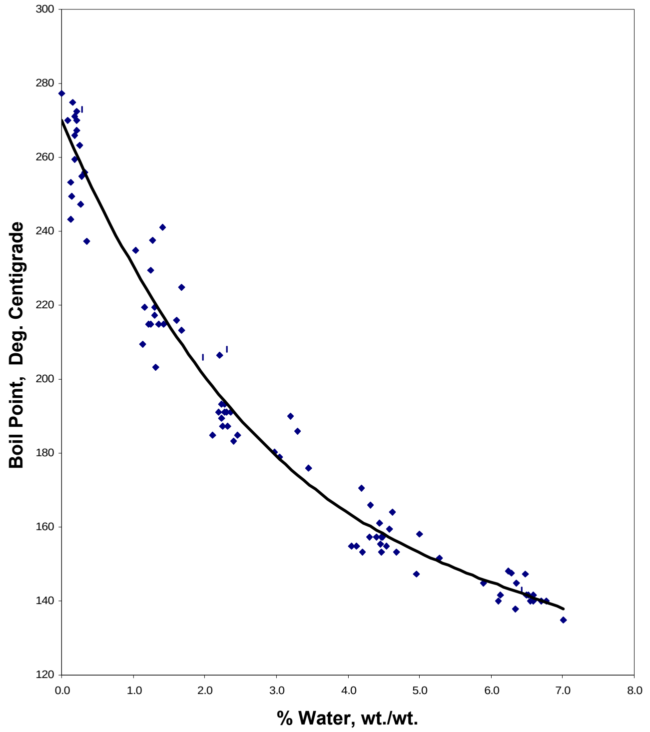
There is no industry consensus on what constitutes good versus bad fluid. The wet boil point is generally accepted as a cutoff point for changing fluid. TUV has stated that the cutoff should be 180°C because fluid in the reservoir generally has less absorbed water and a higher boil point than fluid in the wheel cylinders. The wheel cylinders are located closer to the flexible rubber hoses where most of the water ingression is believed to take place.

The accuracy with which boil point and water content can be measured is open to discussion. This includes results obtained using SAE approved methods. Even with these methods a great deal of variability is seen. The Society of Automotive Engineers Brake Fluid Committee is actively discussing variation in results during wet and dry boil point testing. Typical results of round robin tests at well-known laboratories with experience in testing brake fluid are shown in the attached Figure 1 a & b.

Figure 1 shows a recent ASTM laboratory boil point test on Dow HD 50 brake fluid conducted by SAE at six different laboratories associated with companies that make brake fluid. The results ranged from 280°C to 297°C. 17 Degrees Centigrade variation on a single test fluid when tested by experienced chemists using an approved laboratory method and apparatus. Similarly with Karl Fisher, SAE test results on the same sample at six different laboratories ranged from 2.44 to 3.93. By its nature brake fluid is not an easy substance to measure. Normal data spread in chemical analysis is caused by contamination, operator error, poor storage, loss of calibration, insufficient cooling of the boil type tester, coated electrodes on the Karl Fischer titrator, etc. A list obtained from SAE of probable causes for variation in boil point testing is attached as Figure 2. Some variability in brake fluid analysis data is expected. In the final analysis, the work described here shows this variability does not interfere with the ability of any of the methods used in this study (Karl Fischer, ASTM Boil Point, Refractive Index) to determine good from bad brake fluid.

Results: Boil Point, Karl Fischer % Water, and Refractive Index

Figure 3. Euro DOT 4 New Fluids
With Water Added



The chart in Figure 3 a shows the relationship between % Water and Boil point for 18 new European origin brake fluids with water added. These fluids represent all the DOT 4 fluids specified by European automobile manufacturers and importers. They were sourced from retail automobile sales outlet and service centers, brake fluid manufacturers and automotive supply stores. Figure 3 compares the two SAE and ISO accepted and specified methods - Karl Fischer Titration and Boil Point readings. Both methods are described and approved as ASTM official methods. The results show typical expected variability. Two of the DOT 4 fluids we purchased and tested did not meet the minimum dry boil point specification for DOT 4 fluids. These were not OEM supplied or specified fluids. The two fluids not meeting the specification are not included in the results. The majority of the brake fluids exceed the minimum specs by a large amount. In fact we found most new DOT 4 boils at the 260°C Super Specification.

Figure 4 compares Refractive Index to % Water as determined by Karl Fischer Titration. The trend is decreasing refractive index with increasing water content.

Figure 4. Euro DOT 4 Brake Fluids
New Fluids with Water Added

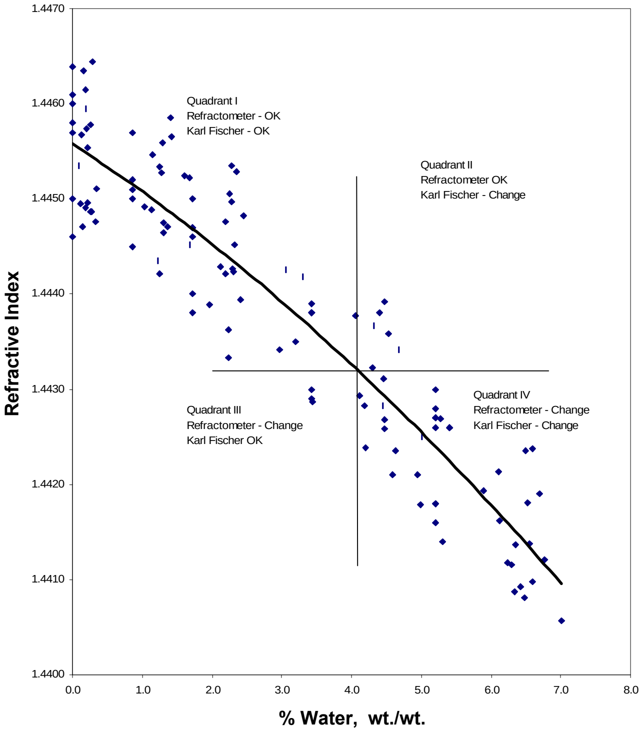


Figure 5 compares Refractive Index to Boil Point as determined by the SAE/ASTM specified methods. The trend is decreasing index with decreasing boil point. The variability seen in Figures 3, 4, and 5 comes from the experimental procedure errors described above plus variability in the various brake fluid formulations. Of the three methods - Karl Fischer, Boil Point and Refractive Index - the refractive index is least likely to contribute to variation due to experimental error. It is by far the least complicated method, requiring only that a sample be placed on the refractometer and read. Boil Point Determinations and Karl Fischer Titrations are much more complicated methods with more room for experimental error.

Figure 5. Euro DOT 4 Brake Fluids
New Fluids with Water Added

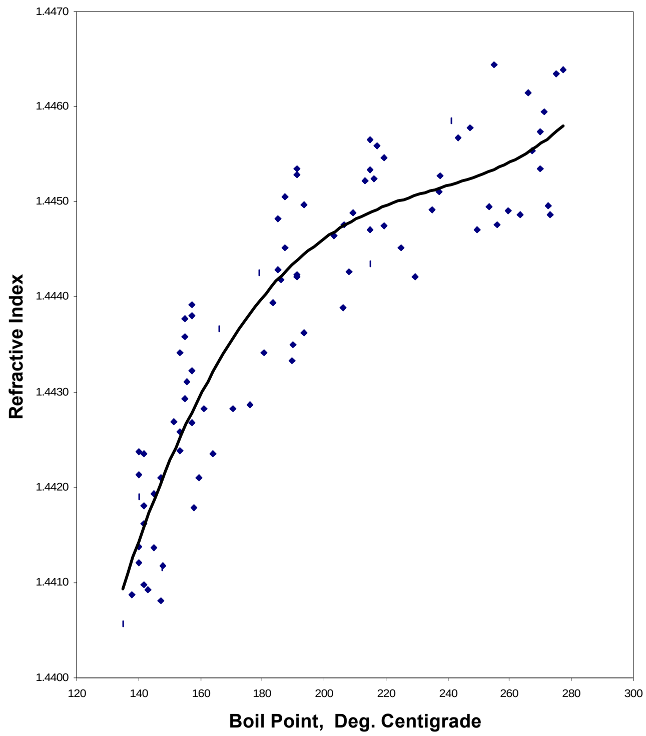
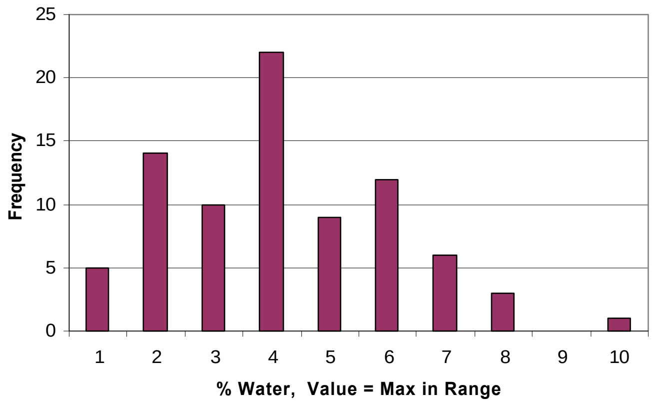


Figure 6 is a histogram showing the amount of water as determined by Karl Fischer titration in the 83 automobile sample taken at the Koln, Germany test center. Obviously many cars in the sample had a great deal too much water in the Brake Fluid. The water content in 53 of the 83 cars was over 4% by weight. Figures 7 a,b,c shows the results of brake fluid testing conducted by Leica at the TUV Vehicle Test Center in Koln Germany. Figure 7a is a comparison graph of the two SAE, ISO and DOT approved methods - ASTM Boil Point Determination and Karl

Figure 6. Koln Brake Fluid Test, N = 83



Fischer Titration. The lines drawn on the graph represent the cutoff for changing fluid -- 180°C (according to the TUV center). TUV recommends changing at 180°C because the sample is normally taken from the master cylinder. They believe 180°C in the master cylinder is equivalent to 155°C at the wheel cylinders. On very few of the 83 cars did the two methods disagree about whether or not to change fluid. If you analyze each sample individually the differences can at times appear quite large. As discussed previously, certain errors are inherent in chemical analysis methods. We can also tell by reviewing boil point versus water content that very few of the 83 cars actually contained Super DOT 4 fluid.

Figure 7b (Refractive Index versus Karl Fischer) shows a comparison of refractive index of the fluid from the sampled vehicles compared to the Karl Fisher Titration results. The obvious trend is a decreasing index as the water content increases. This chart shows the refractive index is a good indicator of the % water content of a random sample of European automobiles. Figure 7c compares refractive index to boil point as determined by the prescribed SAE, ISO and ASTM standards. The trend is decreasing index with decreasing boil point. This chart shows there is very good correlation between the index and boil point. Both figures 7b and 7c show excellent agreement in the determining "good" fluid from "bad". The data shown is also consistent with similar data obtained for new fluids. No adjustments were made for any cars containing Super DOT 4 Fluid. Everything in this study is modeled on the Standard DOT 4 Scale. We are very confident in the refractive index readings. Samples were tested on two different Brake-Chek® hand held brake fluid refractometers and a laboratory refractometer. Excellent correlation was observed between the hand-held refractometer and the laboratory refractometer. Calibration of the laboratory refractometer was verified by reading a certified standard every 0.5 hour.

Figure 7a. TUV Real World Brake Fluid Test
Boil Point Compared to Karl Fischer % Water

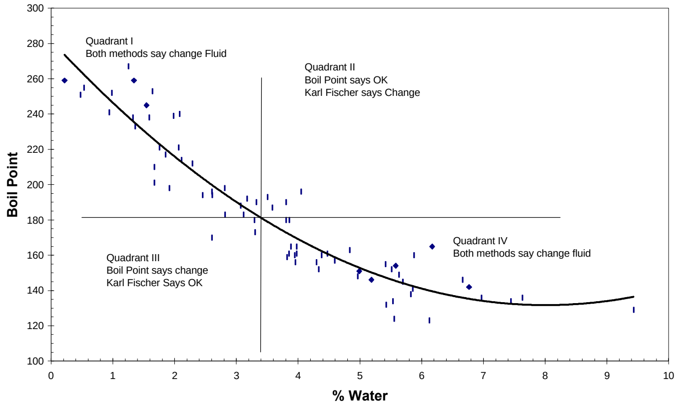


Figure 7b. TUV Real World Brake Fluid Test
Refractive Index Compared to Karl Fischer % Water

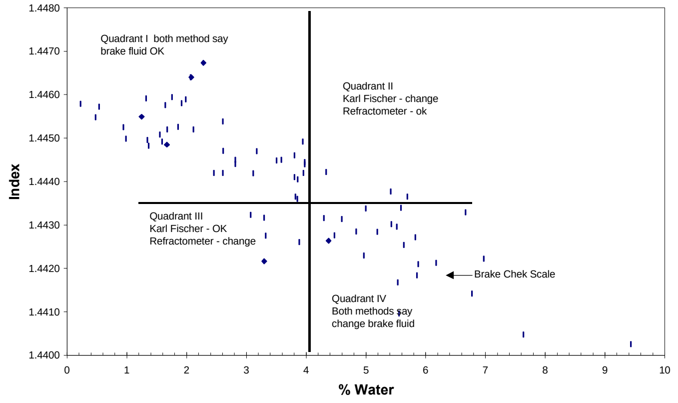
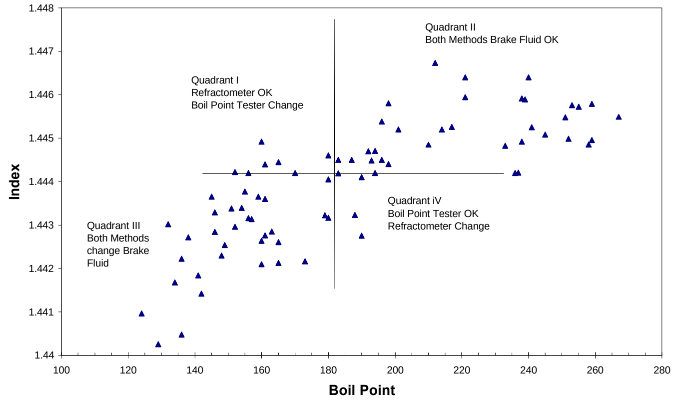


Figure 7c. TUV Real World Brake Fluid Test
Refractive Index Compared to Boil Point



Conclusion

Refractive index is a unique physical property of chemical compounds. It is often specified as an indicator of purity and is used to determine concentration for a wide range of commercial solutions. Measuring refractive index to a high degree of accuracy (+/- 0.00002) is fairly easy and can be easily done with inexpensive handheld devices. Based on a comparison of methods between Karl Fischer titration and temperature corrected refractive index measurements this work has demonstrated that refractive index can be used to determine water concentration in European DOT 4 brake fluids.

To be useful as a field test, the results from brake fluid which has been in service for a period of time must be similar to results obtained on new, clean fluid. In-service fluid is typically darker and may contain particulate contamination. The data from used fluid samples is very similar to the data for the clean, new fluids to which water was added. Contaminants in the used fluid samples appear to have little effect on the Karl Fischer titration or the refractive index measurement. The percent water versus refractive index curve fit for new and used fluids are almost identical.

The safety of a motor vehicle's braking system is directly related to the water content of the brake fluid. As water content increases, the boiling point decreases. Water content in brake fluid increases 1% to 2% per year. A recent study has shown that temperatures of brake fluid in the wheel cylinders of vehicles can reach high enough levels to boil brake fluid containing significant amounts of water. Our study on used brake fluid confirms over 60% of the vehicles tested in Germany had brake fluid with water content above 4%. On the average 4% water reduces the boiling point by 100 degrees centigrade. The brake fluid in the vehicles which tested over 4% water could reach the boiling point under high braking load for short periods or light but continuous braking such as encountered when descending from elevation.

If 4% water as measured by Karl Fischer titration was chosen as a cutoff point for our used vehicle sample the data relating refractive index to % water content shown in Figure 7b would have correctly predicted and agreed on fluid quality in 74 of the 83 vehicles. All of the vehicles in quadrant three of Figure 7b had at least 3% water content. In quadrant 3 the Karl Fisher % water indicates the fluid does not need to be changed but the refractive index does. Figure 7b shows that at most the error in the % water measurement will be 1%. The refractive index versus boil point chart (Figure 7c) shows similar results. The boil tester and refractive index agreed in 75 of the 83 cars tested. The degree of accuracy in predicting whether or not a car requires a fluid change is the same as when the two standard methods, Karl Fischer Titration and Boil Point determination are compared (see Figure 7a). Regular checking of brake fluid by measuring the refractive index with a tool such as the Leica Brake Chek could eliminate a safety hazard represented by vehicles with high moisture content It could also help extend the life of brake system components and reduce maintenance by minimizing corrosion due to high water content. It should also be kept in mind that this study covered the entire population of brake fluids. No corrections were made for DOT 4 versus Super DOT 4 or even DOT 3. The accuracy with which boiling point and % water measurements are estimated by refractometer can be greatly increased by calibrating the Leica Brake Chek to the recommended OEM brake fluid and then checking at regular service intervals at the Dealer. This is the best possible way of assuring safe brake fluid and follows the Society of Automotive Engineers recommendation in Recommended Practice J1707:

> "Whenever the vehicle manufacturer clearly specifies of otherwise indicates the brake fluid required, service maintenance personnel should use the brake fluid recommended by the vehicle manufacturer"

We believe checking brake fluid is even more important in vehicles with "super" fluids formulated to maintain a high boiling point at high water contents. While the boil point of this type of fluid may be in the safe range, there is still a likelihood of corrosion damage or brake system malfunction due to the increase in viscosity caused by high water content.

Figure 1a

Round Robin Boiling Point, F (Dow Chemical HD50 – 4 Brake Fluid)

Procedure		Dow Chemical	Orthene Chemical	ABIC Labs	Case Labs		Castrol	
Standard SAE Method	Run # 1	555, 553	552, 555	560, 558	565, 565,	561, 561	547, 550	
		554, 560	550, 552	562, 562	565, 565	561, 561	550, 552	
	Average	555	552	561	565	561	550	
	Run # 2	552, 555	559, 556	564, 564	555, 555	556, 556	556, 554	
		557, 554	556, 559	563, 562	555, 555	556, 556	552, 552	
	Average	555	558	563	555	556	553	
	Run # 3	559, 560	554, 549	562. 564	559, 559	554, 554	556, 556	
		562, 557	545, 545	564, 563	559, 559	554, 554	558, 556	
	Average	560	548	563	559	554	557	
	Final Average	557	553	562	560	557	553	
Proposed SAE Method	Run # 1	564, 563	553, 550	564, 565	568, 568	564, 564	556, 558	558, 556
		562, 565	550, 550	563, 560	568, 568	564, 564	558, 556	556, 556
	Average	564	551	563	568	564	557	557
	Run # 2	560, 560	556, 556	566, 565	540, 540	536, 536	558, 558	558, 558
		563, 562	556, 556	564, 564	540, 540	536, 536	558, 554	
	Average	561	556	565	540	536	557	558
	Run # 3	562, 564	547, 550	562, 562			558, 558	558, 560
		561, 560	554, 554	560, 562			554, 554	558, 556
	Average	562	551	562			556	558
	Final Average	562	553	563	554	550	557	558

Figure 1B

Exhibit II

SBR Rubber Cups Swell Test At 70°C With and Without Water Added. Using RM- 66-04 Brake Fluid

	Testing Laboratories					
	Case Consulting		Seiken Chemical		Acushnet	
	Dry	Wet	Dry	Wet	Dry	Wet
3 Days						
% Volume Swell	4.77	2.74	4.98	2.66	5.05	2.95
Diameter Change (inches)	0.17	.011	.020	.012	.015	.010
Hardness Change	-1	-3	-1	-3	-9	-7
% Water Content	.35	3.05	.34	3.05	.54	2.44
5 Days						
% Volume Swell	3.97	1.86	3.97	1.86	4.5	2.5
Diameter Change (inches)	.014	.007	.014	.007	.017	.008
Hardness Change	-2	-3	-2	-3	-9	-7
% Water Content	.35	2.99	.35	2.99	.68	2.34
7 Days						
% Volume Swell	3.66	1.64	4.28	1.77	3.9	2.35
Diameter Change (inches)	.013	.006	.016	.008	.017	.008
Hardness Change	-2	-2	-6	-4	-9	-7
% Water Content	.38	2.97	.37	3.18	1.33	2.6
10 Days						
% Volume Swell	3.35	1.46	3.86	1.40	3.4	2.25
Diameter Change (inches)	.012	.005	.014	.006	.012	.008
Hardness Change	-3	-3	-4	-3	-9	-7
% Water Content	.39	2.94	.38	3.13	.52	1.6

Figure 1b (cont'd.)

Exhibit III

SBR Rubber Cups Swell Test At 70°C With and Without Water Added. Using RM- 66-04 Brake Fluid

	Testing Laboratories					
	Castrol		Oxid Inc.		Complex	
	Dry	Wet	Dry	Wet	Dry	Wet
3 Days						
% Volume Swell	5.04	2.89	4.76	2.15	6.41	3.42
Diameter Change (inches)	.019	.010	.017	.007	.015	.007
Hardness Change	-5	-6	-.4	-3		
% Water Content	.35	3.24	.35	3.93		3.00
5 Days						
% Volume Swell	4.71	2.50	4.51	1.26	7.15	4.86
Diameter Change (inches)	.016	.008	.016	.009	.015	.004
Hardness Change	-6	-6	-2	-2		
% Water Content	.35	3.26	.35	4.13		
7 Days						
% Volume Swell	4.32	2.10			5.93	4.79
Diameter Change (inches)	.016	.008			.015	-.004
Hardness Change	-6	-6				
% Water Content	.37	3.31				
10 Days						
% Volume Swell	3.87	1.75	3.57	1.02	5.55	5.10
Diameter Change (inches)	.014	.006	.015	.005	.016	-.004
Hardness Change	-6	-5	-2	-1		
% Water Content	.38	3.30	.35	3.97		

Figure 2

Variables Effecting Wet Boiling Point Results

A. Humidification Procedure

- . Dessicator dimensions (size, volume)
- . Dessicator plate design (hole size)
- . Oven Temperature
- . Placement of test jars within the dessicator
- . Sampling procedure
- . Water determination method
- . Quality of TEGME

B. Boiling Point Variables

- . Size of glass (flask, condenser)
- . Volume of fluid contained in the flask
- . Thermometer calibration
- . Boiling point chips (size, number, water content etc.)
- . Heating method
- . Reflux rate
- . Stabilization time
- . Cooling water temperature
- . Barometric pressure correction
- . Glassware cleanliness (residual brake fluid, water etc.)