A Rudimentary Investigation of Modern Era Potassium Perchlorate Impurities

Eric Hunkins

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Version 2.0

Version History

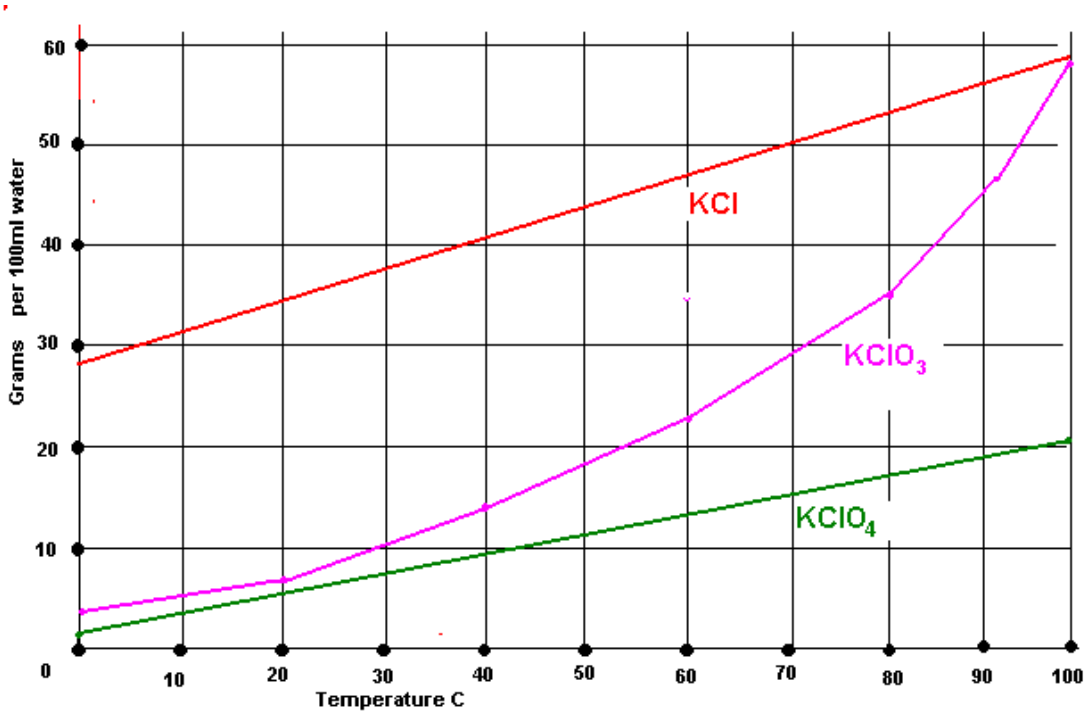
Date	Event	Who
4/23/07	Original Creation	EDH
6/8/07	Added Results of testing Standard Chinese. Added results of flame tests on HP-140 insolubles. Added pictures of Chinese standard sample and a Chinese standard drum.	EDH

Fifteen years ago when I was active in pyrotechnics the first time, the quality of potassium perchlorate never seemed to be an issue. Swedish was the common KCLO4, and it worked well, and nobody thought twice about it. Having recently caught the pyro bug again, I now feel like Rip Van Winkle waking up from a deep sleep and being horrified at what I see. Most of the formulas that I use that have perchlorate in them, were not working the way I remembered them, stars were harder to light, and my favorite purple looked like crap. After hearing similar horror stories from others it started to become obvious that there is something wrong with the currently available KCLO4.

I started this project to re-crystallize one specific grade of perchlorate to use in some of my better color formulas, what I stumbled across convinced me to look into it further. Because of this, I expanded my experimentation to include several other common grades of KCLO4, and collected data as carefully as I could, and included it in this document. This document contains the procedures, the data collected, and some photographs from my experiences re-crystallizing four kinds of modern potassium perchlorate.

The procedure I am using to refine the perchlorate, is based on it's insolubility in cold water (see chart below). The process in a nutshell is to;

1. Heat a bunch of water to 100C (boiling)
2. Dump in an amount of KCLO4 that would represent a saturated solution,
3. Heat it back up to 100C
4. Filter out any insoluble matter
5. Cool it down to 0C (freezing)
6. Filter out the cleaned KCLO4 crystals



1. **Solubility of Potassium Perchlorate in water at various temperatures**

This process has two distinct advantages, one, most of the insoluble matter is removed at the first filtering. The second advantage is that because the sodium and other perchlorates, and chlorates are considerably more soluble in water than KCLO4, most will stay behind in the cooled solution when it is filtered a second time.

It was not my intention to get the highest yield from each batch. The liquor from the initial filtrations could have been boiled down and re-crystallized again to get better yield. The extra cost of energy and labor just didn't seem worth getting the extra 5% or so of perchlorate out of the process. It also wasn't my intention to determine the exact purity of each perchlorate, which would have been impossible with the rudimentary lab equipment that I currently have available.

The process could also have been made more efficient by the using alcohol to help precipitate the perchlorate. KCLO4 is considerably less soluble in alcohol than water. If the second filtrate liqueur was saturated with approximately 50% alcohol, another 5% or 6% of KCLO4 could have been rendered from each batch. Again, the cost of the alcohol, and having to deal with the flammability of alcohol indoors just wasn't worth it for me.

My original plan was to re-crystallize 30 lbs of Chinese high purity HP-140. On processing my first batch I realized there was something terribly wrong. A good portion of the KCLO4 would not dissolve in water. When I noticed the high amounts of insolubles, I changed the procedures to investigate the relative percentage of these insolubles, and to see if I could determine what they were.

The insoluble filtrate I was getting was a dense, very light tan colored powder. Once I dried and weighed the insolubles I was astounded at the percentage of the original KCLO4 contained this material. Over several batches, I tried different temperature combinations and procedures to discover efficiencies in the process. But in all cases, the percentage of insolubles was never below 11% on the HP-140\150.

Since HP-140\150 is extremely free flowing, not like pure or normal perchlorate, and taking into account the density and color of the insolubles, my guess is that the impurity I was seeing is TCP, or TriCalcium Phosphate. TCP is a common anticaking agent used for inorganic oxidizers. TCP is about twice as dense as other anticaking agents used like Sodium Aluminum Fluorite, or Calcium Silicate, and is also denser than the perchlorate itself. In fact, other investigators have already confirmed the presense of TCP causing problems in ammonium perchlorate coming from China in their colored star formulas. Impure forms of TCP also happen to be brownish in color. If it is true, this would certainly explain the problems people have been having with this brand of perchlorate. The addition of large amounts of cheap TCP provide the Chinese with two benefits, one because TCP is denser than perchlorate, they make more money off of every pound they sell over here, and secondly, it makes the perchlorate a nice free flowing powder that is easy to work with, and us dumb Americans fall for it hook line and sinker.

TCP causes many problems for fireworks developers, phosphates are known flame retardants. Ammonium phosphate is used in the match industry to soak the wood sticks in to prevent the flame from propagating down the stick too fast. Calcium is detrimental in fireworks because it has strong orange and red spectral lines in the flame, so the presence of it in any color formulas, other than orange, would wreck most colors in these high percentages. High amounts of TCP could also have an effect on rockets. The pressed grain would less resistant to structural fracture and could lead to additional failures.

2 A beaker of HP-140 that has been filtered and cooled showing the precipitated KCLO4 crystals

Procedures followed;

All HP-140\150 starting material was taken from the center of a brand new drum. The distilled water was purchased at a local grocery store. 1 liter of which was boiled to dryness to confirm that it wasn't adding any insoluble matter. The heated perchlorate solutions of HP-140\150 had a PH of between 6.38 and 6.43 consistently. This low of a PH is unusual but it may be because the TCP is acting as a buffer.

The starting distilled water was put into 4l beakers with a 3 inch magnetic stir bar. The water was then heated to approximately 90C. The starting amount of HP140\150 was added to the heated water. The contents were stirred and heated until the temperature came back up to 100c, about boiling. In the case of the HP-140\150 the solution is mainly clear except for the insoluble matter. The batches were then filtered under vacuum in a 25 cm buchner funnel on a 5 liter vacuum flask. The filter paper and first pass insoluble matter was dried and weighed.

In the first several batches, to make sure all of the perchlorate is out of the insoluble matter, two to three batches of the insoluble matter were put into 3 liters of distilled water and stirred with slight heating for an hour, then filtered under vacuum, and dried

All filtrates were dried at 122F for 6 – 8 hours. Some samples were vacuum desiccated to test the effectiveness of the drying.

After initial filtering for insoluble matter, the liquor was put back into the beakers and put into the beer fridge until it cooled to a temperature of 32 degrees F or 0c. The batches were then filtered to remove the crystallized perchlorate. The filtrate was then dried and weighed.

Once I finished several batches of HP-140 I started to test other grades. Thanks to Dan Creagon who sent me samples of Domestic and Spanish grades to add to the Taiwanese and the HP-140\150 I already had, I was able to process 3 other common types.

Chinese HP-140\150

Batch Number	Starting KCL04 grams	H20 ml	1st Pass Insol grams	Final Insol grams	Yield KCLO4 grams	%Insol	% Yield	%Loss
1	650	3000	?	91.85	483.88	14.13%	74.44%	11.43%
2	650	3000	?	91.85	483.88	14.13%	74.44%	11.43%
3	650	3000	144.10	85.65	479.48	13.18%	73.77%	13.06%
4	650	3000	139.75	85.65	479.48	13.18%	73.77%	13.06%
5	650	3500	135.50	85.65	496.40	13.18%	76.37%	10.45%
6	600	3000		67.15	499.60	11.19%	83.27%	5.54%
7	600	3000		66.10	500.10	11.02%	83.35%	5.63%
8	600	3000		106.75	472.34	17.79%	78.72%	3.49%
9	600	3000		81.34	486.57	13.56%	81.10%	5.35%
10	600	3000		86.54	478.56	14.42%	79.76%	5.82%

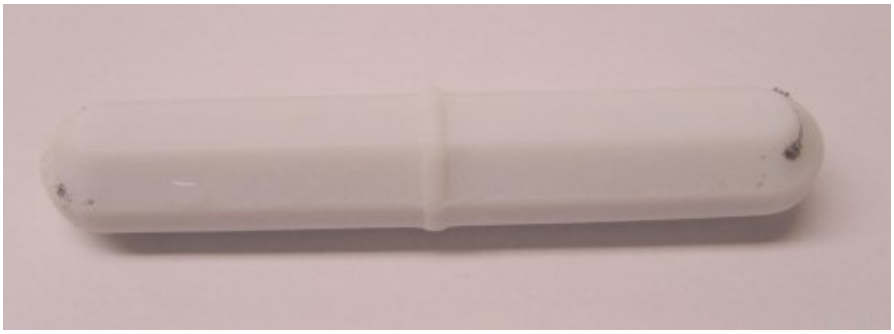
3. The data from processing the HP-140\150

The Domestic.

The Domestic was the worst looking of all the types. The powder straight out of the container had a yellowish brown tinge to it. As you can see from the pictures below. Once it was dumped into the water, the solution looked like chocolate milk. This was also the most difficult perchlorate to process. The fine insolubles plugged up the filter paper quickly and I ended up using up to three circles per batch. The other thing that is troubling about the domestic is that the magnetic stir bar kept coming up with fine metal particles on it. This was obviously Iron, and the brown insolubles in this perchlorate, is most likely iron oxide. Once the insolubles were filtered out the liquor became a yellowish color. I still haven't determined what the yellow contaminate is but the domestic seems to have a healthy supply of it. If it is a sodium compound, it would certainly wreck most color formulas The domestic had a PH of 8.48 in solution.

4**. Domestic after first being dumped in solution at 80c**

5. The domestic after filtering out the insolubles



6 The stir bar with the no extra charge iron filings

7 The insoluble matter on just on one of the three filters from one batch of the Domestic

Domestic								
Batch Number	Starting KCL04 grams	H20 ml	1st Pass Insol grams	Final Insol grams	Yield KCLO4 grams	%Insol	% Yield	%Loss
1	600	3000	NA	45.80	504.50	7.63%	84.08%	8.28%
2	600	3500	NA	62.90	497.97	10.48%	83.00%	6.52%
Total Starting	1200				1002.47			
	2.64317				2.208084			

8**. Data collected from processing the Domestic Perchlorate**

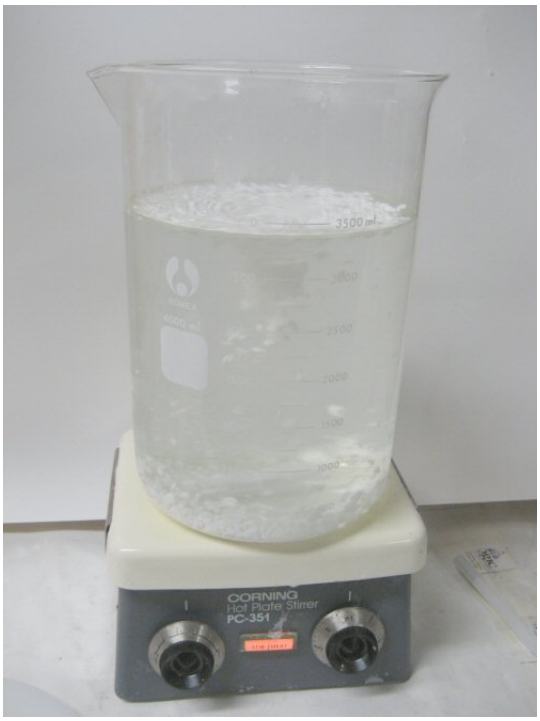
Filtering the insolubles from the domestic was a nightmare. The fine particles size of the brown contaminate clogged the filters quickly, requiring the filter to be changed to continue, which allowed the solution to cool slightly, which then skewed the results. In both batches the percent of insolubles was 7% to 10%, but in reality the actual percentage is probably closer to 2% to 3%. I could have heated the insolubles with water again to make sure all of the perchlorate was out, and gotten a better idea of the exact percentage of the impurity, but this stuff is such a pain to work with that it just wasn't worth extra effort.

After drying the crystals recovered from the cooled filtrate it was clear all of the impurities were not out. About 30% of the crystals were stained a slight yellow color.

The Domestic seems to have three profound impurities, ferrous metal particles, a very fine brown powder, and an extremely fine yellow powder that is slightly soluble in water. The yellow contaminate went though the filters when hot, but some was retained on the filters when cold.

The Spanish

The Spanish seemed to be a lot cleaner. It dissolved into solution quite nicely and had no visible insoluble matter. The water was stained a slight yellow color which is hard to determine from the pictures but there is obviously some contamination. Whatever impurities that the Spanish has, it is soluble in hot water. The first batch was not filtered for insolubles. The Spanish had a PH of 8.23 in solution. Another troubling fact is that the stir bar also contained fine iron particles like the domestic did. With the slight yellow tint, and metal particles, It seems that the Spanish and the Domestic are being made by the same process, but the Spanish seems to be free of most of the iron oxide and only contains the iron filings and the mysterious yellow contaminant.

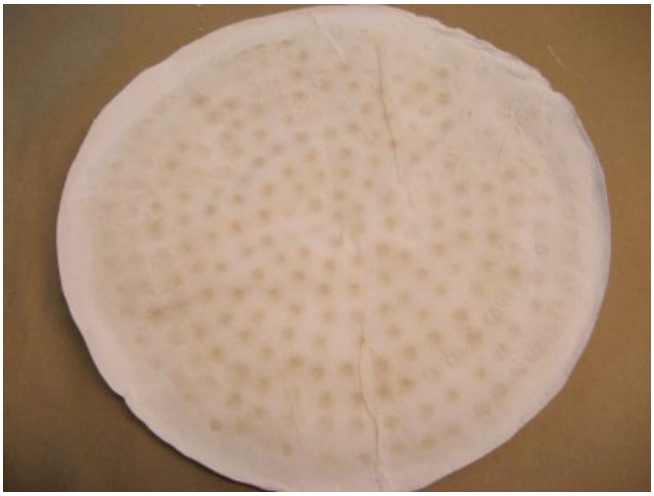


9. The Spanish when first dumped in at 80c

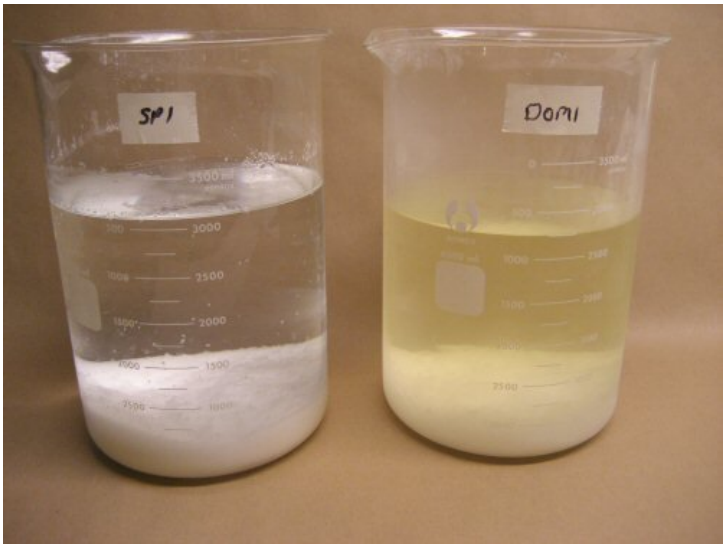
10. Once the temperature comes back up to 100c the solution seems to be free of insolubles with a slight yellow tinge

After the final filtering and drying the crystals from the Spanish had a slight yellow tinge to them also. Since I did not filter the first batch of Spanish for insolubles it is most likely it is the same yellow slightly soluble impurity that is in the Domestic but at a lower quantity. This yellow contaminate has similar properties to potassium perchlorate. It is soluble in hot water but partially insoluble in cold. Because of this it is very hard to remove from the perchlorate. Once it can be identified, a method can be derived for removing it. Processing the second batch of Spanish I decided to filter it for insolubles to see if I could get a sample of the mysterious yellow substance. It seemed to all go through the filter when hot. The only insoluble matter retained was a small amount of brown, and a small amount of an unidentified white compound, with some iron filings. These insolubles only totaled to 1.7% when dried but contained some crystallized

perchlorate so in reality the actual percentage of insolubles is probably closer to .5% to 1%



11. Spanish insolubles at first filtering



12. A batch of Spanish and a batch of Domestic, cooled to 0C just prior to the second filtering

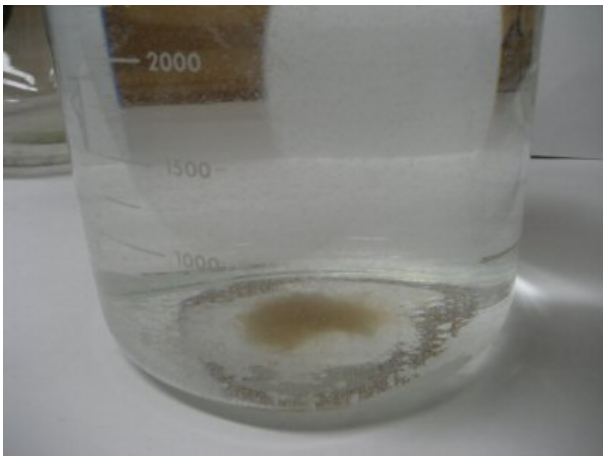
Spanish

Batch Number	Starting KCL04 grams	H20 ml	1st Pass Insol grams	Final Insol grams	Yield KCLO4 grams	%Insol	% Yield	%Loss
1	600	3000	?	NA	576.40	NA	96.07%	3.93%
2	600	3000	?	10.25	574.38	1.71%	95.73%	4.27%
Total Starting	1200				1150.78			
	2.64317				2.534758			

13. Data collected from processing the Spanish

The Taiwanese

The Taiwanese seemed to be a lot like the Spanish. At 100c it was mainly clear without a lot of visible insolubles. The stir bar did contain about the same amount of metal filings as the Spanish and the Domestic. When I stopped the stirring and was about ready to filter I noticed that a brown cloud had formed in the center. I hadn't noticed this in the Spanish and there would have been no way I could have seen it in the domestic. The pictures are a bit deceiving because when filtered, it turned out to be such a small amount that it wouldn't show up very well in the images.



14. Taiwanese at 100c with the light brown cloud

15. The metal filings on the Taiwanese stir bar

16. The Taiwanese at 100C ready to filter

17. The Taiwanese filter

In general the Taiwanese was the best of the four. There was no mysterious yellow contaminate that showed up when the solution was cooled. In solution it was mostly clear. The Taiwanese only contained the metal filings and an almost undetectable amount of the fine brown contaminate. The returns from crystallization are what I would expect from a good perchlorate.

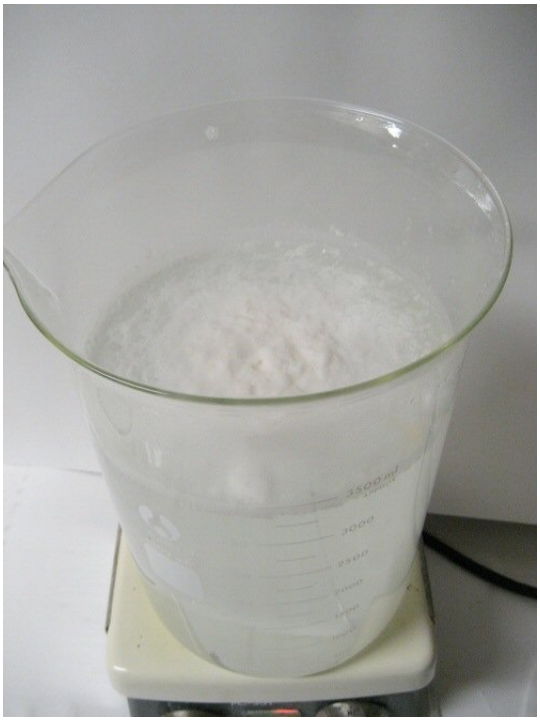
Taiwanese

Batch Number	Starting KCL04 grams	H20 ml	1st Pass Insol grams	Final Insol grams	Yield KCLO4 grams	%Insol	% Yield	%Loss
1	600	3000	?	NA	574.98	NA	95.83%	4.17%
2	600	3000	?	NA	576.34	NA	96.06%	3.94%
Total Starting	1200				1151.32			
	2.64317				2.535947			

18. Data collected from processing the Taiwanese

Chinese standard

A kind person sent me enough Chinese standard to run two batches. From my observations, physically, the Chinese standard looked almost identical to the HP140\150. It was fine white, free flowing powder. Processing it was almost identical to the HP140\150. It made a clear solution with the light tan colored powder floating on top. What became obvious is that this Chinese standard contained far less of the suspected TCP that was in the HP140\150. There was also no metal filings on the stir bar like there had been in some of the non Chinese brands. The returns on the re-crystallization also showed better results than the HP_140\150.



19. The standard Chinese at 100 with a tan powder floating on top

Chinese Standard

Batch Number	Starting KCL04 grams	H20 ml	1st Pass Insol grams	Final Insol grams	Yield KCLO4 grams	%Insol	% Yield	%Loss
1	550	3000	NA	35.35	512.35	6.43%	93.15%	6.85%
2	550	3000	?	37.40	508.65	6.80%	92.48%	7.52%
Total Starting	1100				1021.00			
	2.42291				2.248899			

20. Data collected from processing the Chinese standard

Conclusions

Generally I am leaving the conclusions to those that review this document, but for my personal view. It is clear to me that HP-140\150 and the Domestic have no place in fireworks, they are simply polluted with too many of the wrong impurities to be useful for anything other than bottom shots. The Spanish and the Taiwanese seem to be better and could be used for everything other than color sensitive formulas like blues and purples. The Chinese standard also seemed better than the HP-140\150 at least when it came to the amount of TCP in it. In the case where you want to make a decent blue or purple with today's available perchlorates, there seems to be no choice but to re-crystallize your own.

Safety and Process Tips

If you are going to re-crystallize some perchlorate yourself, here are some tips that may help you.

1. Get decent equipment! Get a real hot plate with a magnetic stirrer. Trying this on the stove or on a normal hotplate would be very dangerous. Saturated solutions change heat very quickly. Without stirring the solution it could boil at the bottom but still be cold on top. This would cause an almost explosive boiling condition that could get you hurt. Use only heavy wall Pyrex beakers. The ones you seen in these pictures are not heavy wall and I was scared every time I touched one. I have since gotten heavy wall ones. If you have a beaker break while handling it you will get splashed with 100C plus saturated solution and you will most likely die of shock before reaching the hospital. Normal glass will break while being heated, only Pyrex or the equivalent, is safe to heat like this.
2. Where safety gear. Eye and face protection. Being splashed in the eyes with a hot oxidizer will lead to certain blindness. Sometimes your eyes can be saved when splashed with a mild acid, they cannot be saved when splashed with this stuff. Where a protective apron! If you have an accident this will save you from a horrible death.
3. Hot perchlorate solutions have the potential to start fires on contact with organic materials! If you are working on a wooden bench, cover it with a heavy plastic. Move any flammable materials out of the area and have a fire extinguisher ready. You almost certainly won't be able to put out a perchlorate fed fire, but there is a slim chance you might be able to save the lab. Wipe up all spills! You will have spills
4. Build a trap to catch hot liquid in your vacuum line. The hot vapor will carry through your lines to your vacuum pump and destroy it. I had to rebuild my pump twice during the course of these experiments even with a nice big home built trap.
5. Make a blanket for your beakers. I used a blanket cut from a water heater blanket that you can by at the hardware store. This blanket will help keep the temperature even from the top to the bottom of the beaker and will also reduce the heating time.
6. Spend the bucks on decent filter paper. Most filter papers cannot handle the heat, the vacuum, and the oxidizing material. If you use cheap paper it will disintegrate almost instantly, leaving you with a mess that is impossible to fix until you get decent filter paper.

Flame test on the impurities from the HP_140\150

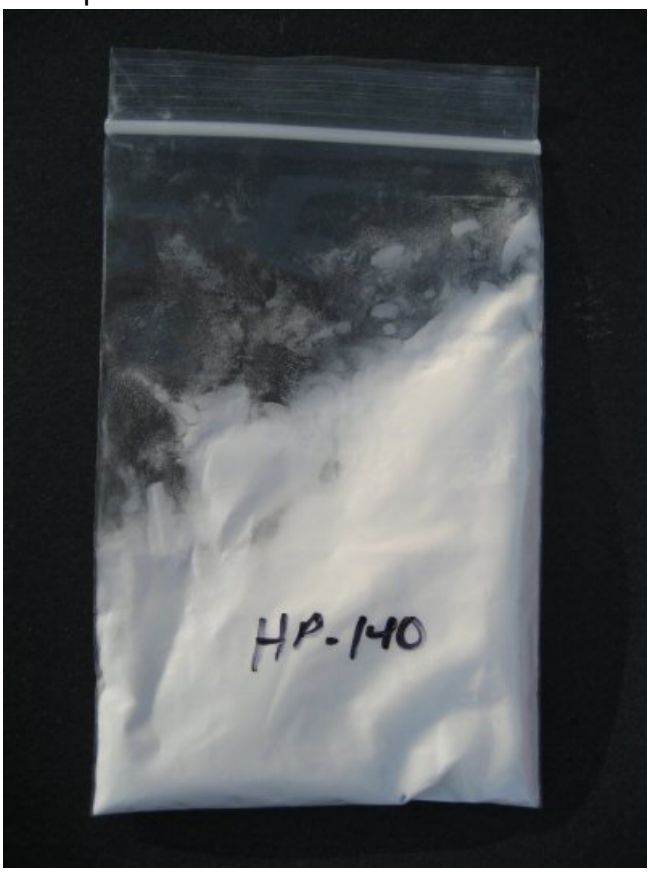
As part of the impurity guessing process, I decided to do a flame test on some of the HP-140\150 impurities. My first inclination was to ram a bunch into a tube and then peal away the paper and torch the pellet to see what color would come up. After having several tries at it only to see it crumble away when I rolled the paper off, duh, it hit me, this is anti-caking agent it isn't going to ram easily. I then decided to get a stainless steel wire and make a loop. The first picture below show the loop in a MAP gas flame without any contaminate on it (Map gas burns blue). The second shows the loop with contaminate in the flame. It clearly burns orange. To me this is a good indication of calcium. If it were perchlorate you would see a blue to lilac color, sodium would be more towards the yellow.

21. The base flame test on a bare stainless loop

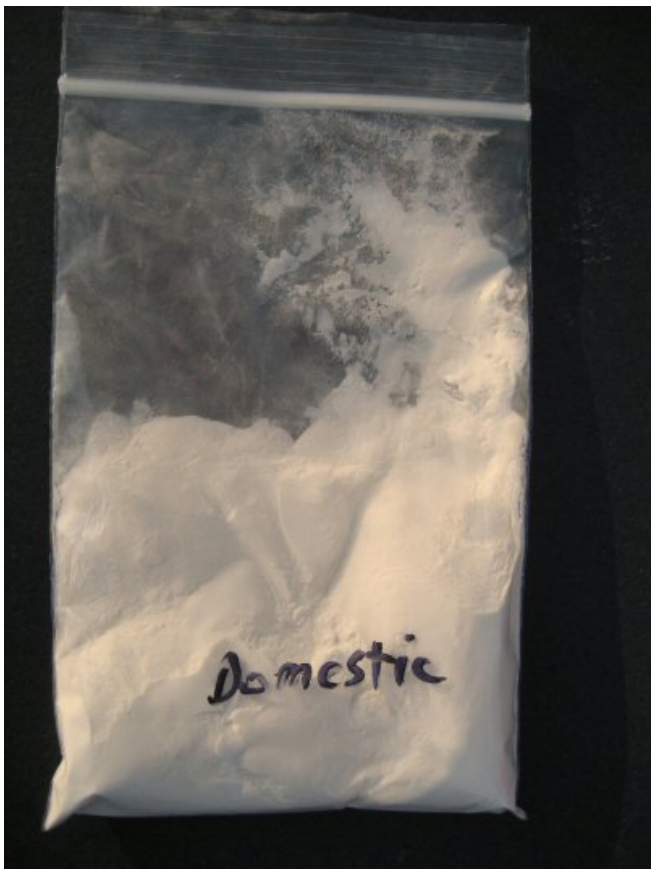
22. The flame test on the HP-140\150 impurity

Some miscellaneous pictures

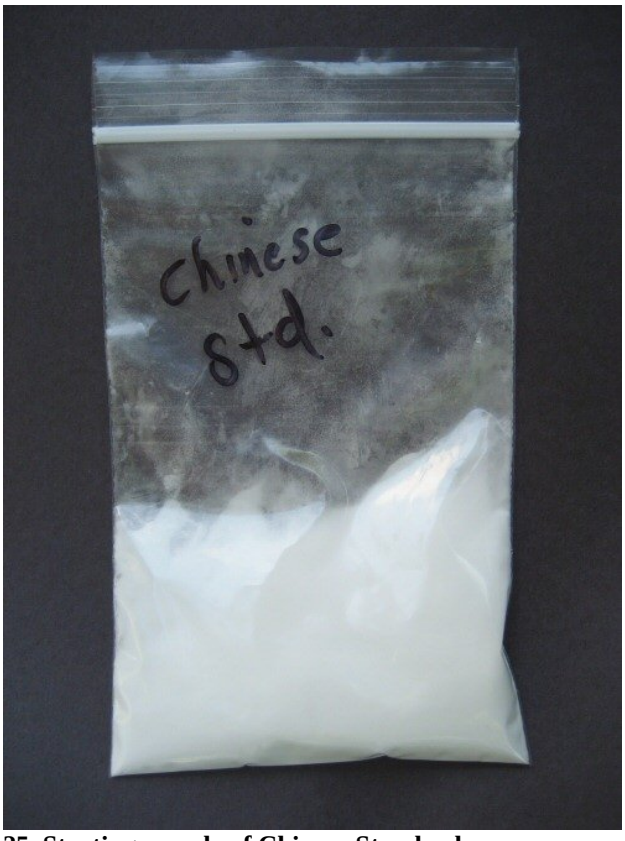
Samples



23 Starting Sample of HP-140



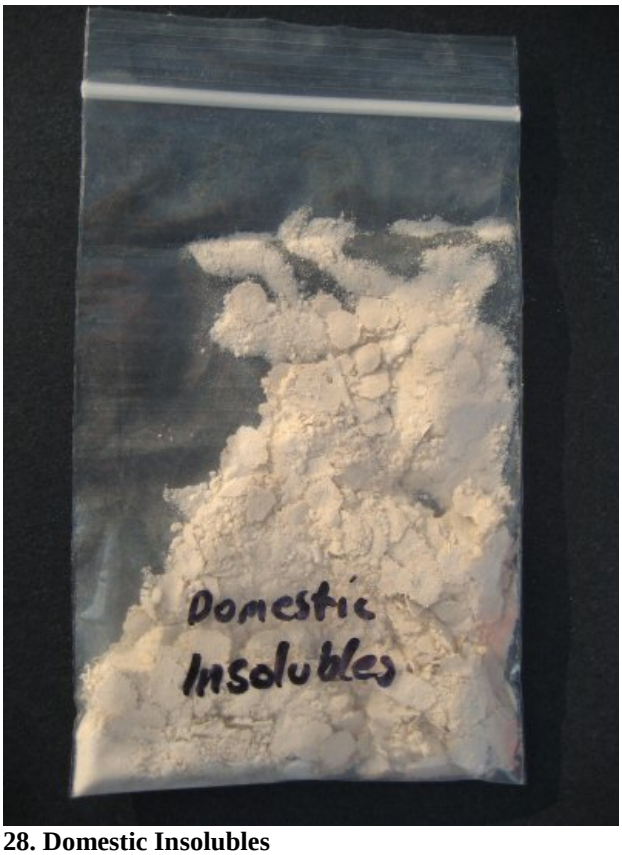
24**. Starting sample of the domestic**



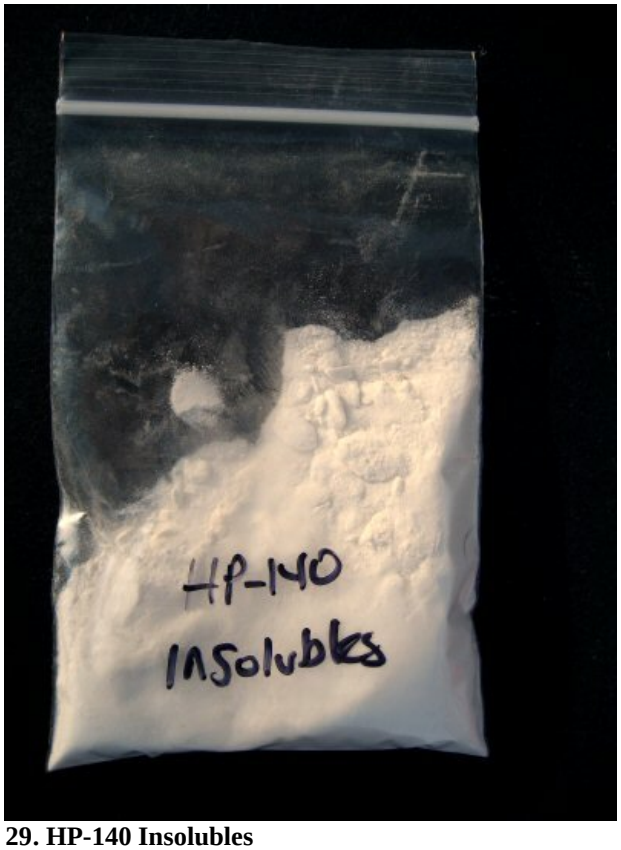
25. Starting sample of Chinese Standard

26. The Spanish

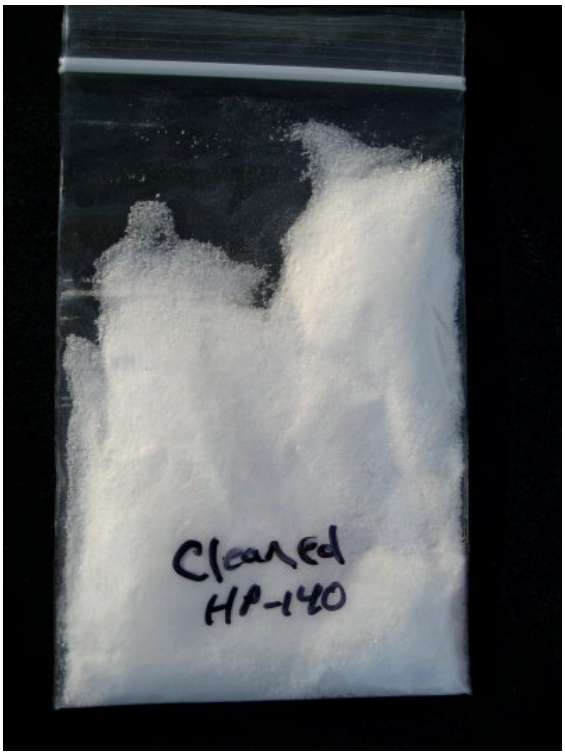
27. The Taiwanese



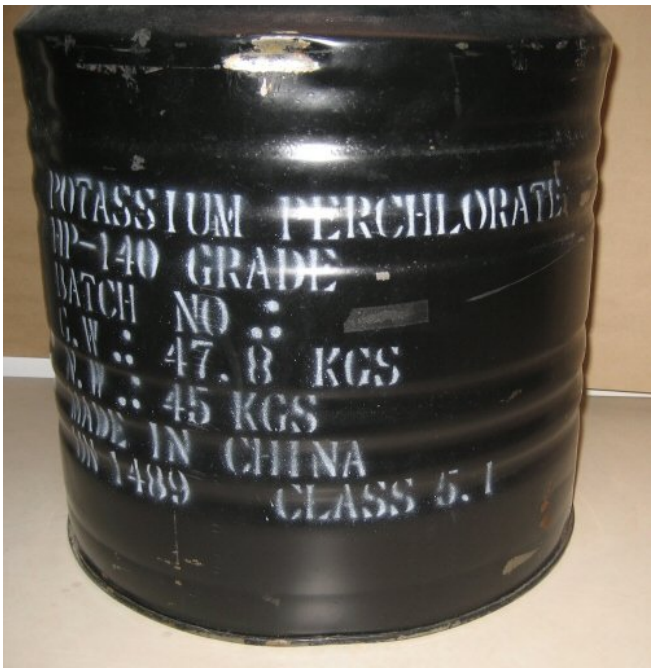
28. Domestic Insolubles



29. HP-140 Insolubles

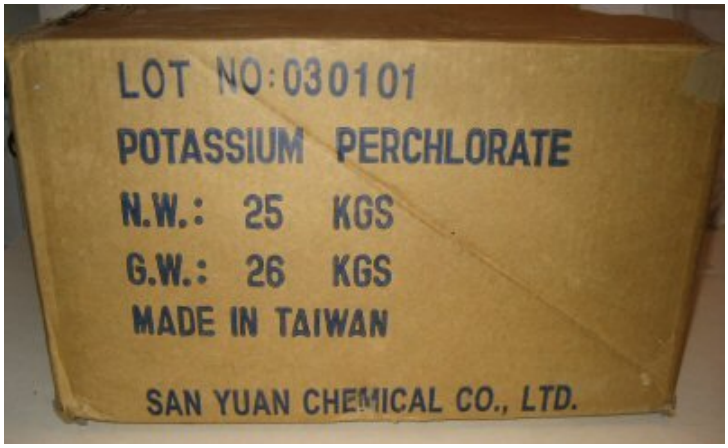


30. Cleaned HP-140



31. Picture of an HP-140 drum

32. Picture of a Chinese Standard drum



33. Taiwanese Perchlorate Packaging