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MICROENCAPSULATION OF LITHIUM

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Final Report covering 12 February 1985 through 31 December 1985

Prepared for:

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Highly reactive micronized lithium metal was successfully encapsulated under this program. The encapsulated lithium dramatically increases the shelf-life and decreases the associated hazards of the elemental lithium. Experimental procedure required that the encapsulation be performed in an inert atmosphere (lithium powder readily reacts with water, nitrogen, oxygen, etc.) and that non-reactive coating materials be developed.

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EXECUTIVE SUMMARY

U.S. Army Belvoir Research and Development Center funded Southwest Research Institute (SwRI) to encapsulate micronized lithium metal. The program began on 12 February 1985 and was completed on 31 December 1985.

SwRI successfully encapsulated micronized lithium metal and delivered three samples of one pound each of various matrix material coatings for evaluation by U.S. Bureau of Mines. One of these matrix materials was selected by U.S. Army Belvoir Research and Development Center for the ten-pound sample.

Encapsulation procedures were performed in an inert atmosphere and non-reactive coating matrix materials were developed. Analytical results showed that encapsulation dramatically increased the shelf-life and decreased the associated hazards of elemental lithium.

The dry micronized lithium metal used in the microspheres was cleaned at SwRI from a lithium dispersion. A supplier for dry micronized lithium metal was found, but particle size specifications were not able to be met (less than 105 micron lithium particles were required to prepare 500 micron microspheres).

Analytical payload determinations were found to have a large standard deviation (±10% of true value). It is recommended if future lithium encapsulation programs are funded, that monies be directed towards analytical methods development.

Under this program, standard operating procedures were developed to safely encapsulate micronized lithium metal. Future programs to prepare more lithium microspheres can be completed for less cost per pound due to streamlining production and using established operating conditions.

Recommendations for additional encapsulation development include studying dual coatings of the microspheres to improve shelf-life characteristics, optimization of payload and matrix material, and improving reproducibility of the analytical results.

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INTRODUCTION

PICCOLYTE

This is the final report documenting the technical aspects of Contract DAAK70-85-C-0008, Southwest Research Institute (SwRI) Project 01-8529 for the encapsulation of micronized lithium metal. Elemental lithium is very reactive with both oxygen and water, forming the oxide upon reaction with oxygen and forming the hydroxide and hydrogen upon reaction with water. This metal also reacts with nitrogen to form the nitride.

The U.S. Army Belvoir Research and Development Center requires protection of elemental lithium from reactive species (especially oxygen) during mixing and storage operations of lithium in explosives. Furthermore, it is required that the detonation not be hindered by the coating material.

SwRI used microencapsulation technology to develop a protective coating for elemental lithium. The coating material studied was a blend of wax, Piccolyte®, and polyethylene known to have good water barrier properties and combustion characteristics. SwRI prepared microspheres from a dispersion of micronized lithium metal in a matrix material (the protective barrier). Figure 1 is an enlarged schematic view of one such microsphere.

The process to form microspheres is carried out in an inert atmosphere to prevent the micronized lithium metal from reacting prior to encapsulation. A slurry is prepared of micronized lithium metal in the matrix material and is fed to the center of a rotating disk. Liquid microspheres are sprayed off the disk periphery and solidification of the matrix material occurs by cooling during the fall prior to impact with the collection area. After collection and size separation operations, the microspheres are ready for evaluation.

Microsphere size is controlled by feed material viscosity and disk speed. Viscosity can be controlled by slurry temperature, matrix composition, and slurry solids content. A schematic of the rotating disk forming microspheres is presented in Figure 2.

Analytical results included elemental lithium content, total lithium ion concentration, shelf-life characteristics, and particle size distribution. Developed methods, analytical results, and encapsulation procedures are presented in this report.

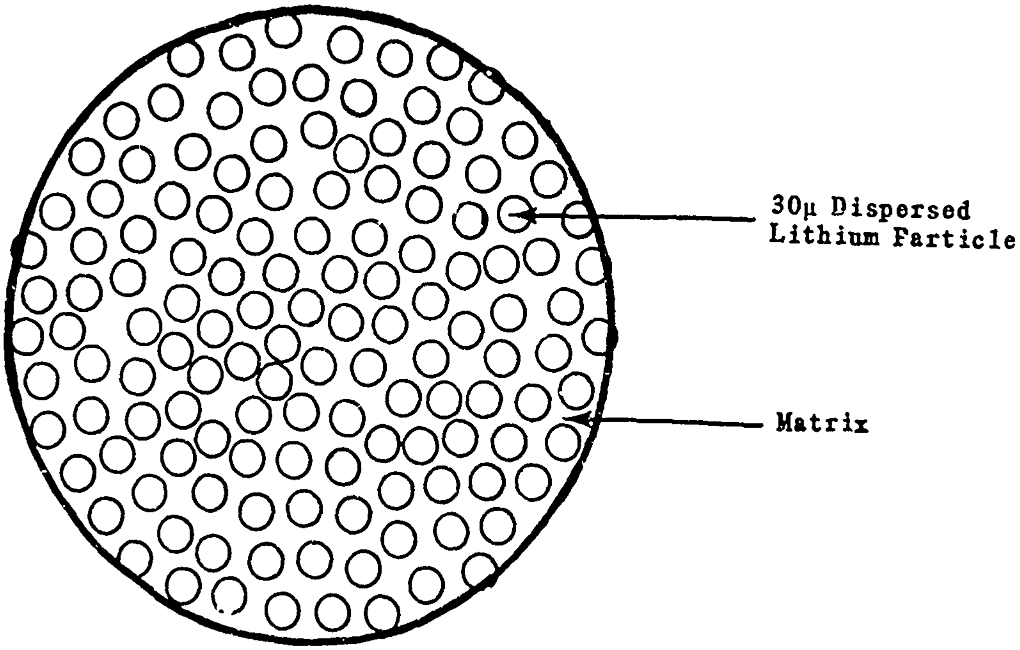


Figure 1. Enlarged View of 500 μ, 36% Payload Microsphere.

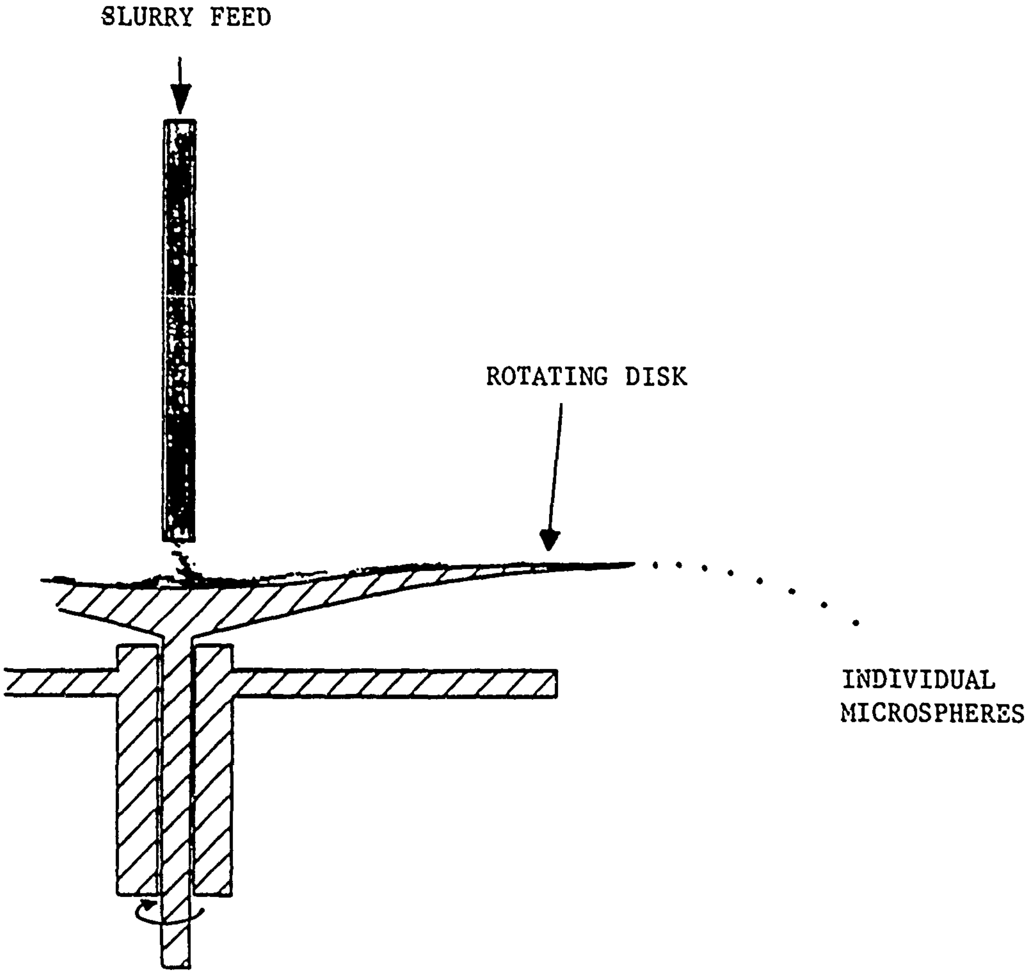


Figure 2. Schematic View of Formation of Microspheres From the Rotating Disk.

EXPERIMENTAL PROCEDURE

To effect safe operation with the micronized lithium metal and to provide an inert atmosphere to the microsphere preparation, a multi-section enclosure was built. Figure 3 is a side view of the enclosure. The encapsulation area is eight feet by eight feet by eight feet and has three view windows made from Plexiglas® (two are on the side walls and one is in the roof). Both front panels of the two glove boxes are also made from Plexiglas®.

For safety, all interior walls, floors, and ceilings were constructed of Sheetrock® to discourage the spread of a fire. Sealing of each enclosure was accomplished by caulking all seams and applying two coats of epoxy paint to all interior surfaces. Personnel safety details not shown in Figure 3 include side rails and kick-plates around the work platforms and a back staircase.

In the early part of the program, it was believed that the only way micronized lithium metal could be supplied was in a 30% solids dispersion of mineral oil. Thus, the dispersion was purchased and the lithium metal was cleaned by extracting the mineral oil with n-pentane. This operation and subsequent weighing procedures were carried out in the Preparation Area Glove Box under an argon atmosphere. See Appendix A for standard operating procedures used for the cleaning of the lithium dispersion.

Later in the program, one manufacturer was found who could supply micronized lithium metal. Size specification for this material was -140 mesh, in other words, all particles were required to be less than 105 microns. Cost savings could be realized by purchasing dry micronized lithium metal since the cleaning operations of the 30% solids dispersion of mineral oil could be eliminated. Unfortunately, the manufacturer was unable to meet product specifications. Of the micronized lithium metal supplied to SwRI, 41.5% was greater than 500 microns (+35 mesh). Microspheres could not be made using this material (refer to Encapsulation Run Number 4-3 in Table 6). No other suppliers of dry micronized lithium metal have been found.

The primary matrix materials used were various compositions of paraffin wax, Piccolyte®, and polyethylene. The paraffin used was Boler 1426. Piccolyte® is prone to gradual oxidation, so fresh samples with an anti-oxidation additive were used. Hercules supplied Piccolyte A-115 BHT for this program. The polyethylene used was Eastman Chemical Products' Epolene C-16. Product specification sheets

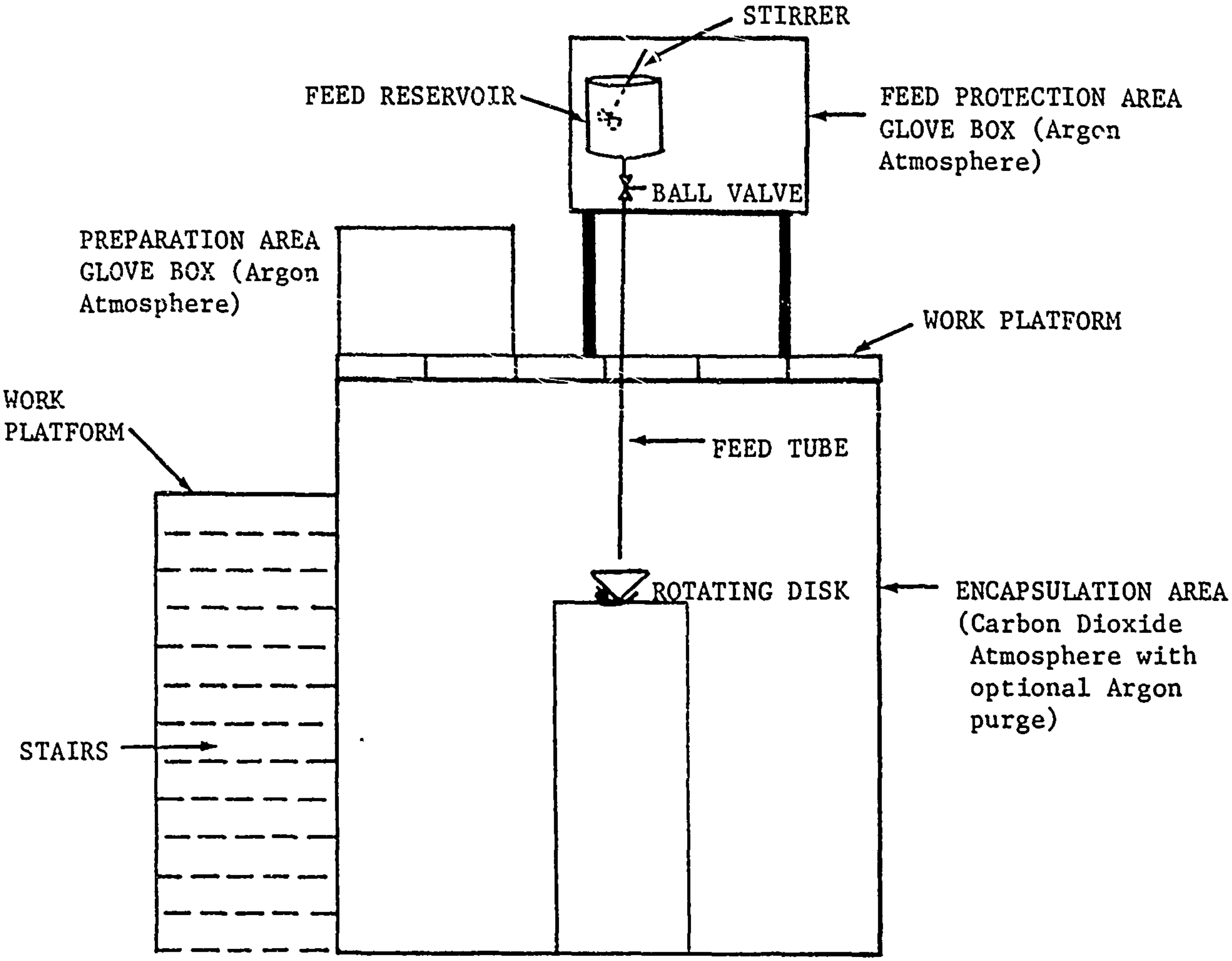


Figure 3. Side View of Enclosure Built to Provide an Inert Atmosphere for Encapsulation of Lithium Metal.

for these raw materials and the certificate of analysis of the lithium metal dispersion are presented in Appendix B.

Preparation of the matrix blend was performed under a nitrogen blanket to discourage oxidation of the Piccolyte®. The paraffin wax was melted at 190°F and then heated to 240°F, the polyethylene melting point. Polyethylene was then added to the paraffin wax as a solid, melted, and mixed. Holding the temperature constant, Piccolyte® was then added to the mixture as a solid, melted, and blended. This hot matrix blend was then poured onto a pan to rapidly solidify as a thin sheet. After solidification, the sheet is broken into flakes which are weighted and packaged for the encapsulation process.

Preweighed quantities of micronized lithium metal and matrix are introduced in separate sealed containers to the Feed Protection Area. This glove box is then sealed and purged with argon gas. When the oxygen content of the glove box is below 1%, the argon purge is decreased to provide a 0.1 inches of water positive pressure in the Feed Protection Area. The preweighed matrix is then added to the feed reservoir and melted. The temperature of the melt is then held at 250°F (approximately 100°F below the melting point of lithium) and the preweighed micronized lithium metal is added to the feed reservoir. With approximately one hour of stirring, a homogeneous dispersion is prepared and ready to feed to the rotating disk for encapsulation. The ball valve on the feed tube is then opened. The dispersion of micronized lithium metal in the melted matrix is thus gravity fed to the hot rotating disk. Liquid microspheres are sprayed off the disk periphery and solidification of the matrix occurs by cooling during the fall prior to impact with the collection area. After collection and size separation operations, the microspheres are ready for evaluation.

The rotating disk is located in the Encapsulation Area. A carbon dioxide atmosphere was selected for this area in lieu of argon for several reasons. Lithium metal is protected in the Encapsulation Area by its dispersion in the matrix, so the need for a truly inert atmosphere is not imperative (carbon dioxide reacts with elemental lithium at elevated temperatures). Furthermore, by feeding liquid carbon dioxide to the Encapsulation Area, the collection zone can be rapidly cooled and maintained at a low temperature to encourage rapid solidification of the matrix. Finally, carbon dioxide is much less expensive than argon.

In the event that a hazard would develop in the encapsulation area, or the carbon dioxide began to react with the lithium, then the optional argon purge would be utilized.

As stated earlier, the standard operating procedures used for this program are presented in Appendix A. Analytical methods were developed during this program to determine total lithium ion and elemental lithium contents in a sample of microspheres. Total lithium ion content was determined by standard ion chromatographic methods. The method developed and sample data sheet for determination of elemental lithium content is presented in Appendix C.

Experimental efforts to select the optimum matrix material and operating conditions began by mixing several different compositions of a matrix material composed of paraffin wax, Piccolyte®, and polyethylene. In addition, microcrystalline wax was substituted for paraffin wax and polybutene was substituted for polyethylene. Non-reactive formulations were evaluated by shell barrier properties, tackiness, and payload. Promising materials were used for encapsulation trials.

Mixtures having low viscosity were selected for simulant trials to determine operating conditions (i.e., proper disk speed, feed temperature, and feed rate). The dispersed particles for the initial simulant trials were titanium dioxide. Prior to work with the micronized lithium metal, selected shell materials were analyzed on a Fourier Transform Infrared Spectrophotometer (FTIR) for oxidation. Oxidized materials were not used as matrix materials for micronized lithium metal since these would react with the elemental lithium.

Microspheres were evaluated by appearance, particle size distribution, payload, and shelf-life characteristics. Microsphere appearance was used to qualitatively evaluate matrix coating properties. Highly reactive lithium microspheres were dark gray, less reactive lithium microspheres were light gray to off-white in color. Representative samples of microspheres were classified by size range to obtain particle size distributions.

Lithium metal content of the microspheres was determined by gas evolution (procedure is presented in Appendix C). The residual solution from this procedure was extracted with deionized water and total lithium ion concentration in the aqueous extract was determined using ion chromatography. The difference in these two values indicate the extent of loss of elemental lithium during the encapsulation process.

Shelf-life characteristics were determined by aging selected samples at 23°C, 50% relative humidity (R.H.) and 55°C, 9% R.H. for various periods of time. The aged samples were then analyzed for elemental lithium content.

Based upon payload and reproducibility of a given experimental trial, three systems were selected to produce one-pound samples. These three samples of one pound each were shipped to the U.S. Bureau of Mines for evaluation.

As requested by U.S. Army Belvoir Research and Development Center, the matrix material for the ten-pound sample was 45% paraffin wax, 45% Piccolyte®, and 10% polyethylene; the theoretical payload was 35.7%. Again, simulant trials were made to determine operating conditions. However, this time Dry-Flo starch was the dispersed material since it has a density closer to that of lithium than does titanium dioxide. After establishing the operating conditions and analyzing the matrix by FTIR, ten pounds of encapsulated micronized lithium metal were produced.

RESULTS

The multi-section enclosure for the production of the lithium microspheres proved to be a good concept, and a few modifications were made during the program to increase ease of working with micronized lithium metal. Safety monitoring devices were proven adequate and backup safety devices were successful.

Polybutene was found to be too stringy and too low melting to use in the matrix. Microcrystalline wax was a good substitute for paraffin wax. A one-pound sample of microspheres using microcrystalline wax was not made since it was theorized that the microcrystalline wax structure would tend to be less protective than the paraffin wax.

Numerous materials were screened for compatibility with lithium and for physical properties required by the microencapsulation process. Five matrix compositions were selected for additional testing; these materials are listed in Table 1 with their respective microencapsulation run numbers.

The microspheres made during those trials were analyzed for elemental lithium content and compared to the theoretical (as determined from weighed quantities of raw materials) lithium content. In a few instances, total lithium ion content was also obtained by analytical procedures. The results of these determinations are presented in Table 2. Particle size distribution data and operating conditions for encapsulation runs are presented in Tables 3, 4, 5, and 6.

It was determined that some of the low elemental lithium payloads obtained on batches with 34% theoretical lithium content was a result of a nonhomogeneous dispersion of micronized lithium metal in the matrix material.

Shelf-life tests in constant humidity chambers indicated that encapsulated elemental lithium remained stable for several days. In comparison to encapsulated elemental lithium stored in a closed container which had full activity after three months, the constant humidity chamber results were disappointing.

Results of shelf-life testing on Sample 2-12 are graphically presented in Figure 4. Within sixteen hours of testing, Sample 2-12 reacted faster at 55°C, 9% relative humidity (R.H.) than at 23°C, 50% R.H. After sixteen hours of testing, an inversion was noted where reaction dramatically increased for the 23°C, 50% R.H. case and slowed for the 55°C, 9% R.H. case. In fact, at

TABLE 1. MATRIX MATERIALS USED FOR MICROENCAPSULATION OF LITHIUM

Matrix Composition by Weight Percent				
Paraffin Wax	Microcrystalline Wax	Piccolyte®	Polyethylene	Associated Run Numbers
80	0	10	10	1-2, 2-5, 2-10, 2-11, 2-13
75	0	15	10	2-4, 2-6, 2-12
70	0	20	10	1-4, 2-9
45	0	45	10	1-1, 2-8, 2-14, 2-15, 3-1, 3-2, 4-1, 4-2, 4-4, 4-5, 4-7, 4-8, 4-9
0	80	10	10	2-7

TABLE 2. LITHIUM CONTENT IN PREPARED MICROSPHERES SEPARATED BY MATRIX MATERIAL

Run	Weight Percent of Lithium		
Number	Theoretical	Elemental	Total Ion
2-5	40.0	30.4	40.0
2-10	32.0	25.3	-
2-11	32.0	30.2	-
2-13	32.0	26.2	-
2-4	40.0	27.8	40.2
2-6	34.0	30.9	-
2-12	34.0	24.0	-
2-9	34.0	22.1	35.6
2-8	35.7	28.6	-
2-14	34.0	28.3	-
2-15	32.0	28.6	-
4-1	35.7	35.4	-
4-2	35.7	35.5	-
4-4	35.7	35.8	-
4-5	35.7	36.6	-
4-7	35.7	31.7	-
4-8	35.7	29.2	-
4-9	35.7	36.1	-
2-7	40.0	28.0	-

TABLE 3. OPERATING CONDITIONS AND PARTICLE SIZE DISTRIBUTIONS FOR SIMULANT (TITANIUM DIOXIDE) MICROSPHERE TRIALS USING THE ELECTRICALLY-POWERED DISK

Parameter	Run Number 1-1	1-2	1-3	1-4
Matrix	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene	80% Paraffin Wax 10% Piccolyte® 10% Polyethylene	70% Paraffin Wax 20% Piccolyte® 10% Polybutene	70% Paraffin Wax 20% Piccolyte® 10% Polyethylene
Theoretical Payload	28.6%	16.7%	16.7%	16.7%
Approximate Feed Rate (grams/minute)	51	200	200	200
System Temperatures (°F)				
Feed Reservoir	194	205	203	219
Feed Tube	194	160	149	158
Encapsulation Area	72	75	70	76
Disk Speed (RPM)	1040	1040	1040	1040
Particle Size Distribution				
>1000 μ	0.2%	0%	0%	0%
710-1000 μ	3.8%	0.1%	0.3%	0%
425-710 μ	64.6%	20.4%	33.5%	8.0%
212-425 μ	30.7%	77.2%	59.0%	77.2%
<212 μ	0.7%	2.3%	7.2%	14.8%
Comments	Stringing. Unstable dispersion.	Feed tube plugged. No stringing. Tacky microspheres.	Feed tube plugged. No stringing.	Feed tube plugged.

TABLE 4. OPERATING CONDITIONS AND PARTICLE SIZE DISTRIBUTION FOR MICRONIZED LITHIUM MICROSPHERE TRIALS USING THE ELECTRICALLY-POWERED DISK

	Run Number			
Parameter	2-1	2-2	2-3	2-4
Matrix	70% Paraffin Wax 20% Piccolyte® 10% Polyethylene	Unknown	Durkee 17	75% Paraffin Wax 15% Piccolyte® 10% Polyethylene
Theoretical Payload	34.6%	25.9%	38.2%	40%
Elemental Lithium Determination				27.8%
Approximate Feed Rate (grams/minute)	Unknown	135	N/A	38
System Temperatures (°F)				
Feed Reservoir	189	284	N/A	265
Feed Tube	Unknown	Unknown	N/A	180
Encapsulation Area	60	62	N/A	55
Disk Speed (RPM)	1500	1900	N/A	1740
Particle Size Distribution				
>1000 μ	22.7%	Unknown	N/A	>1000 μ 0.2%
710-1000 μ	4.5%			850-1000 μ 5.8%
425-710 μ	4.4%			425-850 μ 83.9%
212-425 μ	54.4%			212-425 μ 9.6%
<212 μ	14.0%			<212 μ 0.5%
Comments	Slightly too viscous feed.	Unstable dispersion.	Run failed due to shell reaction with lithium.	Tacky microspheres.

...continued

TABLE 4. (CONTINUED)

Parameter	Run Number			
	2-5	2-6	2-7	2-8
Matrix	80% Paraffin Wax 10% Piccolyte® 10% Polyethylene	75% Paraffin Wax 15% Piccolyte® 10% Polyethylene	80% Microcrystalline Wax 10% Piccolyte® 10% Polyethylene	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene
Theoretical Payload	40%	34%	40%	35.7%
Elemental Lithium Determination	30.4%	30.9%	28.0%	28.6%
Approximate Feed Rate (grams/minute)	67	109	40	56
System Temperatures (°F)				
Feed Reservoir	260	300	270	300
Feed Tube	185	250	175	250
Encapsulation Area	48	38	32	50
Disk Speed (RPM)	Unknown	1380	1360	1300
Particle Size Distribution				
>1000 μ	0.4%	0.1%	2.2%	0.1%
850-1000 μ	9.3%	0.2%	7.0%	0.1%
425-850 μ	89.7%	88.4%	81.6%	75.7%
212-425 μ	0.5%	10.0%	9.1%	21.2%
<212 μ	0.1%	1.4%	0.1%	2.9%
Comments		Good run.	Erratic flow to disk. Very high viscosity.	Feed tube plugged due to poor cleaning procedure. Some stringing. Microsphere collection zone was 2-1/2 ft in radius.

...continued

TABLE 4. (CONTINUED)

Parameter	Run Number 2-9	2-10	2-11	2-12
Matrix	70% Paraffin Wax 20% Piccolyte® 10% Polyethylene	80% Paraffin Wax 10% Piccolyte® 10% Polyethylene	80% Paraffin Wax 10% Piccolyte® 10% Polyethylene	75% Paraffin Wax 15% Piccolyte® 10% Polyethylene
Theoretical Payload	34%	32%	32%	34%
Elemental Lithium Determination	22.1%	25.3%	30.2%	24.0%
Approximate Feed Rate (grams/minute)	59	125	100	135
System Temperatures (°F)				
Feed Reservoir	300	300	280	275
Feed Tube	215	250	220	200
Encapsulation Area	50	46	46	45
Disk Speed (RPM)	1330	1300	1560	1380
Particle Size Distribution				
>1000 μ	0.1%	3.0%	1.6%	0.2%
850-1000 μ	0.0%	8.5%	0.3%	0.2%
425-850 μ	94.3%	78.8%	66.8%	95.3%
212-425 μ	3.9%	9.4%	28.4%	3.8%
<212 μ	1.7%	0.3%	3.0%	0.7%
Comments	Good run.	Microspheres impacted well. Nonnhomogeneous dispersion.	Little stringing. Microsphere trajectory is 2 ft in radius.	Few microspheres impacted walls.

...continued

TABLE 4. (CONTINUED)

Parameter	Run Number 2-13	2-14	2-15
Matrix	80% Paraffin Wax 10% Piccolyte® 10% Polyethylene	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene
Theoretical Payload	32%	34%	32%
Elemental Lithium Determination	26.2%	28.3%	28.6%
Approximate Feed Rate (grams/minute)	239	85	83
System Temperatures (°F)			
Feed Reservoir	290	300	300
Feed Tube	190	185	200
Encapsulation Area	48	42	42
Disk Speed (RPM)	1760	1420	1580
Particle Size Distribution			
>1000 µ	0.2%	0.9%	0.4%
850-1000 µ	1.1%	8.0%	0.0%
425-850 µ	91.7%	82.4%	94.5%
212-425 µ	6.7%	8.5%	3.5%
<212 µ	0.3%	0.2%	1.6%
Comments	Few microspheres impacted walls. Tacky microspheres.	Few microspheres impacted walls. Tacky microspheres.	Some stringing. Good collection.

TABLE 5. OPERATING CONDITIONS AND PARTICLE SIZE DISTRIBUTIONS FOR SIMULANT (DRY-FLO STARCH) MICROSPHERE TRIALS USING THE ELECTRICALLY-POWERED DISK

	Run Number		
Parameter	3-1		3-2
Matrix	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene		45% Paraffin Wax 45% Piccolyte® 10% Polyethylene
Theoretical Payload	35.7%		35.7%
Approximate Feed Rate (grams/minute)	180		341
System Temperature (°F)			
Feed Reservoir	230		320
Feed Tube	185		220
Encapsulation Area	50		50
Disk Speed (RPM)	1360		Unknown
Particle Size Distribution			
		>1180 μ	1.2%
>500 μ	5.4	850-1180 μ	2.0%
355-500 μ	14.5%	710-850 μ	65.2%
<355 μ	80.1%	600-710 μ	5.8%
		500-600 μ	13.9%
		425-500 μ	3.8%
		355-425 μ	2.8%
		<355 μ	5.3%
Comments	Stringing initially. Raised temperatures to minimize stringing.		Many microspheres impacted walls. Increased RPM to minimize this impact.

TABLE 6. OPERATING CONDITIONS AND PARTICLE SIZE DISTRIBUTION FOR MICRONIZED LITHIUM MICROSPHERE TRIALS USING THE ELECTRICALLY-POWERED DISK

	Run Number			
Parameter	4-1	4-2	4-3	4-4
Matrix	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene
Theoretical Payload	35.7%	35.7%	35.7%	35.7%
Elemental Lithium Determination	35.4%	35.5%	N/A	35.8%
Approximate Feed Rate (grams/minute)	45	45	N/A	57
System Temperatures (°F)				
Feed Reservoir	270	300	N/A	290
Feed Tube	150	175	N/A	250
Encapsulation Area	40	44	N/A	52
Disk Speed (RPM)	1340	1360	N/A	1300
Particle Size Distribution				
>1180 µ	3.0%	1.7%	N/A	0.02%
850-1180 µ	0.1%	0.2%		0.03%
710-850 µ	0.1%	0.1%		0.07%
600-710 µ	0.3%	0.3%		10.43%
500-600 µ	17.0%	13.5%		41.98%
425-500 µ	72.7%	39.0%		19.44%
355-425 µ	0.8%	13.6%		17.18%
<355 µ	5.9%	31.6%		10.86%
Comments	Initial temperatures were too cold. >600 µ was primarily strings. Microsphere trajectory was 2 ft. in radius. 87.8% product yield.	>600 µ was primarily strings. 87.8% product yield.	Feed tube clogged. Cause determined was that lithium powder supplied by Alfa products did not meet size specifications.	

...continued

TABLE 6. (CONTINUED)

Parameter	Run Number				
	4-5	4-6	4-7	4-8	4-9
Matrix	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene	45% Paraffin Wax 45% Piccolyte® 10% Polyethylene
Theoretical Payload	35.7%	35.7%	35.7%	35.7%	35.7%
Elemental Lithium Determination	36.6%	N/A	31.7%	29.2%	36.1%
Approximate Feed Rate (grams/minute)	57	Unknown	>47	Unknown	26
System Temperatures (°F)					
Feed Reservoir	275	295	265	300	270
Feed Tube	260	270	280	260	255
Encapsulation Area	52	56	40	30	35
Disk Speed (RPM)	Unknown	1360	1320	1300	1300
Particle Size Distribution					
>1180 μ	0.33%	N/A	0.05%	0.74%	7.37%
850-1180 μ	0.08%		0.11%	1.40%	3.74%
710-850 μ	0.07%		0.16%	4.46%	4.72%
600-710 μ	0.24%		1.16%	24.28%	10.67%
500-600 μ	0.49%		52.82%	38.84%	22.95%
425-500 μ	52.30%		22.22%	12.26%	25.84%
355-425 μ	25.20%		9.34%	7.56%	12.93%
<355 μ	21.28%		14.14%	10.47%	11.79%
Comments		Problem with resistance heater. No product collected.	Used induction heater for disk.	Used induction heater for disk.	Used induction heater for disk. Batch size was 1/3 that of previous runs-decreased head pressure shows significant drop in feed rate.

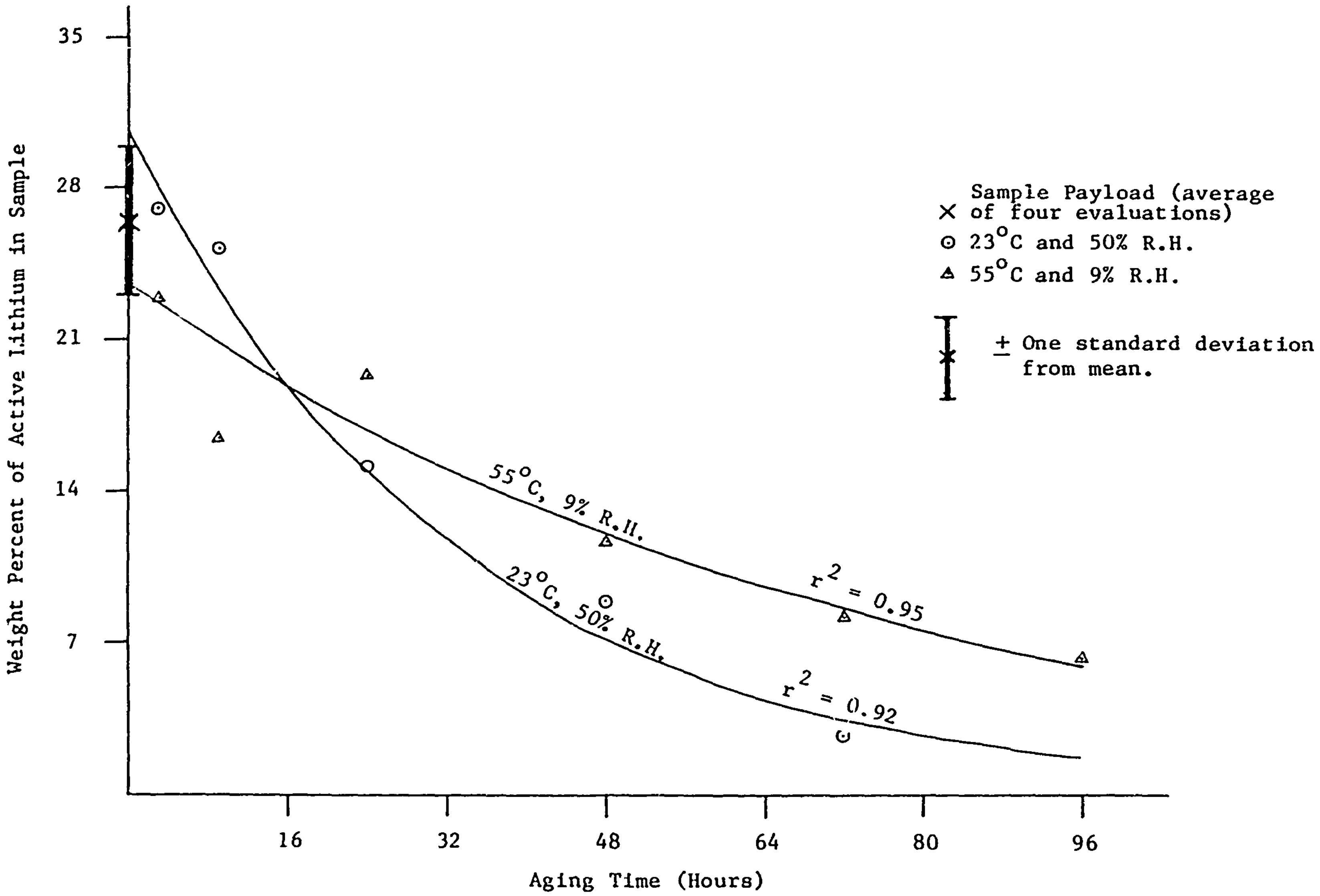


Figure 4. Shelf-Life Results for Sample 2-12 Reported as Weight Percent of Elemental Lithium in Sample

ninety-six hours, the sample at 55°C, 9% R.H. was analyzed as still containing 6.3 weight percent of elemental lithium and the sample at 23°C, 50% R.H. contained a negligible amount of elemental lithium.

The elemental lithium contents in microspheres were statistically evaluated with no evidence of statistical significance among alternate treatments (matrix, well dispersed micronized lithium metal in matrix prior to encapsulation, and theoretical payload). Summaries of statistical results are presented in Table 7.

The first deliverable, three encapsulated lithium samples of one pound each, were shipped to the U.S. Bureau of Mines, Bruceton Research Center, Attention: Mr. Ed Hay, for testing on October 10, 1985. These were shipped in three 5-gallon metal drums each containing approximately one pound of encapsulated lithium. Attached to each drum was a material safety data sheet for lithium metal and Lithium Corporation of America's Product Bulletin describing handling, storage, and safety precautions. These attachments are presented in Appendix D.

The metal drum weights were as follows:

Container Number	Total Weight	Sample Weight	Active Ingredient Weight
1 of 3	10 lbs	495 grams	132 grams
2 of 3	10.5 lbs	541 grams	154 grams
3 of 3	9 lbs	459 grams	128 grams

Container 1 of 3 holds Sample A consisting of
195 grams from Run 2-6
300 grams from Run 2-12

Container 2 of 3 holds Sample B consisting of
189 grams from Run 2-8
124 grams from Run 2-14
228 grams from Run 2-15

Container 3 of 3 holds Sample C consisting of
206 grams from Run 2-11
253 grams from Run 2-13

The sample from each drum was stored in a plastic-coated (shatter-proof) jar sealed under argon. Thus, two jars each were in containers 1 of 3 and 3 of 3, and three jars were in container 2 of 3.

The second deliverable, a ten-pound sample of encapsulated lithium, was shipped on December 31, 1985 to the U.S. Bureau of Mines for testing. This sample was composed of the following lots:

Run Number	Sample Weight
4-1	795.8 grams
4-2	798.4 grams
4-4	838.8 grams
4-5	818.3 grams
4-7	507.8 grams
4-8	734.5 grams
4-9	193.5 grams
TOTAL	4,687.1 grams = 10.33 pounds

TABLE 7. STATISTICAL RESULTS OF ELEMENTAL LITHIUM CONCENTRATIONS FROM VARIOUS TREATMENTS FOR ENCAPSULATED LITHIUM

Test	Source of Variation	Sum of Squares	d.f.	Mean Square	F Ratio	Result
ANOVA for matrix	Between treatments	33.53	4	8.38	1.30	Not significant (P>25%)
	Within treatments	45.07	7	6.44		
ANOVA for well dispersed runs	Between treatments	8.51	1	8.51	1.15	Not significant (P>25%)
	Within treatments	44.20	6	7.37		
ANOVA for theoretical payload	Between treatments	11.23	3	3.74	0.44	Not significant (P>25%)
	Within treatments	67.28	8	8.41		

DISCUSSION

Shelf-life stability in constant humidity chambers did not reach expectations, even though microspheres can be stored for long periods of time in sealed containers. The reactant was not determined on this program; it is assumed that water vapor was the reactant and that at the higher storage temperature, the matrix softened permitting the encapsulated lihtium to react more readily.

Microscopic examination of the microspheres showed a very thin matrix coating on surface lithium particles. Water was placed on the microscopic slide and initial reactions were observed at these sites. A calculation of the maximum theoretical percent lithium concentration in a microsphere based upon the closest packing of the lithium spheres with an ideal diameter of 30 microns in a larger sphere of 500-micron diameter determined 68.9% as the maximum theoretical payload. This packing geometry dictates that all lithium particles are in contact with each other and that the matrix only fills the voids. Due to surface tension, this packing geometry is unrealistic. Nevertheless, the lithium microsphere payload of 36% is very densely packed; refer to Figure 1 of the scale model of this situation. Diffusion path lengths through the microsphere outer coating in some instances are less than one micrometer.

The micronized lithium metal readily reacts at the sites closest to the microsphere surface. Onc reacted, these sites become pathways for further reactions within the microsphere. Furthermore, a dramatic viscosity increase with increasing lithium content was observed. It is known that high viscosity adversely affects microsphere formation. This could be an additional reason that poor barrier properties are observed for microspheres containing greater than 40% by weight of lithium.

Separation of the micronized lithium particles from the lithium metal-mineral oil dispersion did not alter the lithium particles; extraction of mineral oil at room temperature under argon atmosphere with n-pentane (inert to lithium) theoretically will not affect the lithium. No agglomerates were observed in the lithium powder and no lithium degradation was seen in the analytical results of elemental lithium content. Thus, a second coating on the microsphere surface or a lower lithium content in the microsphere will result in a longer diffusion pathlength for water, oxygen, etc. and consequently a longer shelf-life in constant humidity chambers.

Consequently, a second coating was applied to a small sample of lithium microspheres. This second coating was Saran, a good moisture barrier material. Shelf-life testing results showed some improvement. Visual observations indicate that the Saran coating slightly increased the shelf-life in the constant humidity chambers. Shelf-life testing results for the Saran coating and the control are presented in Figures 5 and 6.

It is obvious from the payload analysis data that many questions remain unanswered including the maximum micronized lithium metal payload, the optimum matrix, and the tremendous variability among microencapsulation trials.

It has been hypothesized that statistical significance among various treatments of preparation of encapsulated lithium may not have been found due to analytical procedure sensitivity, in other words, the width of the population distribution expected by the analytical procedure may be too great to observe treatment variations. To test this hypothesis, replicate samples from the same population were taken in the same manner as those samples for determining elemental lithium content. A standard deviation equivalent to 13.4% of the elemental lithium mean was obtained (Table 8 contains the data for these trials).

Ion chromatography produced a high degree of precision among the data for determining the total lithium ion concentration in a given sample. To improve the precision with the gas evolution method for determining elemental lithium content, multiple replicates per determination can be done, but is a very costly approach. A more reasonable approach which was pursued was to identify the source of variation. It is believed that selection of representative samples of a given run is the source of variation.

The total lithium ion content uniformity by ion chromatography in a given run is primarily a function of the degree of uniform dispersion of lithium in the matrix material prior to encapsulation. The precision of elemental lithium content by gas evolution method is a function of both total lithium ion content and particle size distribution. Since the replicated samples show good uniformity of the total lithium ion content, it can be assumed that a good dispersion was made. Furthermore, the elemental lithium content variations may be the result of a non-representative particle size distribution in the analytical grab sample.

For example, the smaller microspheres probably react more quickly than the larger microspheres since the smaller ones will have a greater surface to

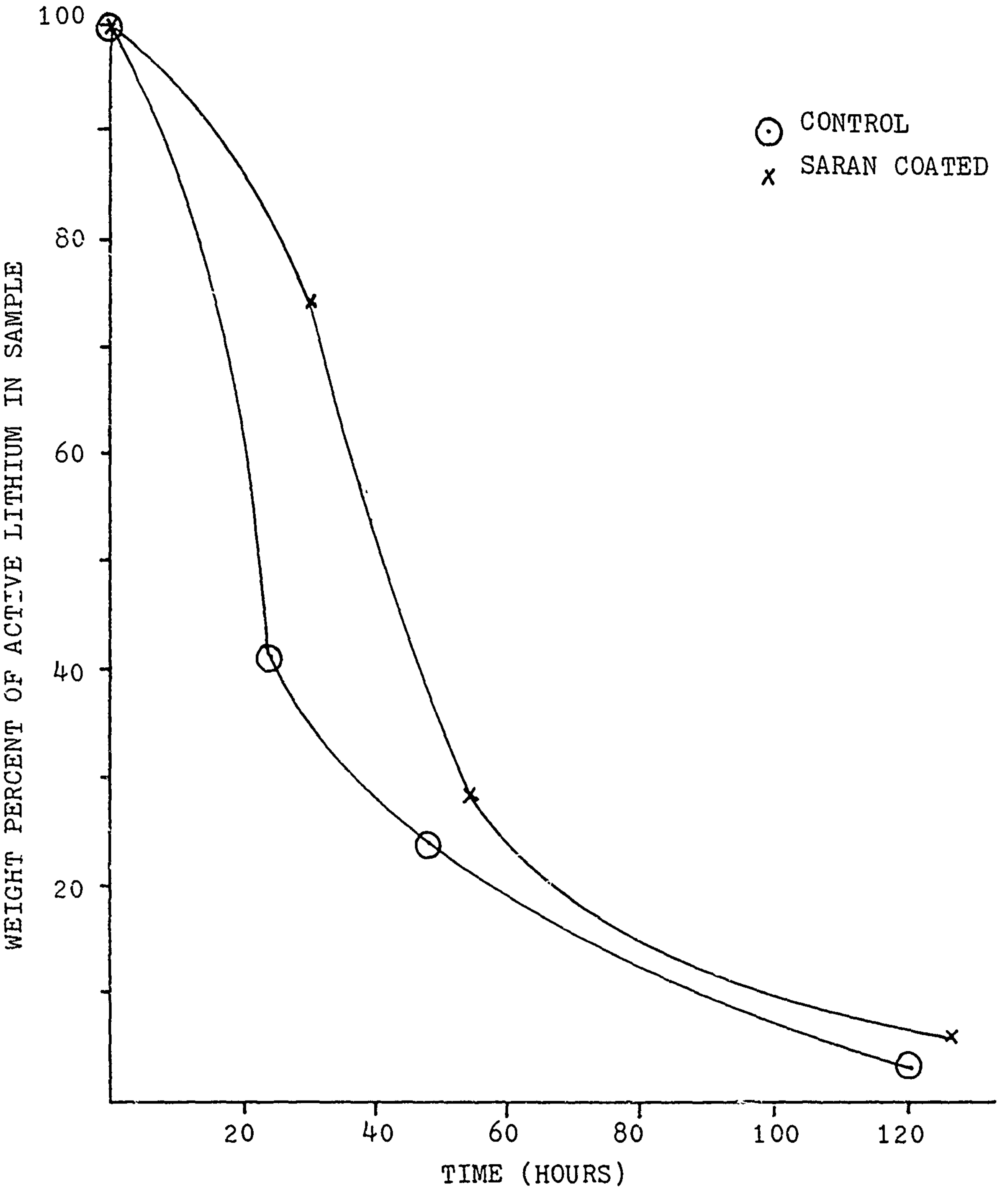


Figure 5. Effects of Saran Coating on Run 2-1 Reported as Active/Payload*100% at 23°C and 50% R.H.

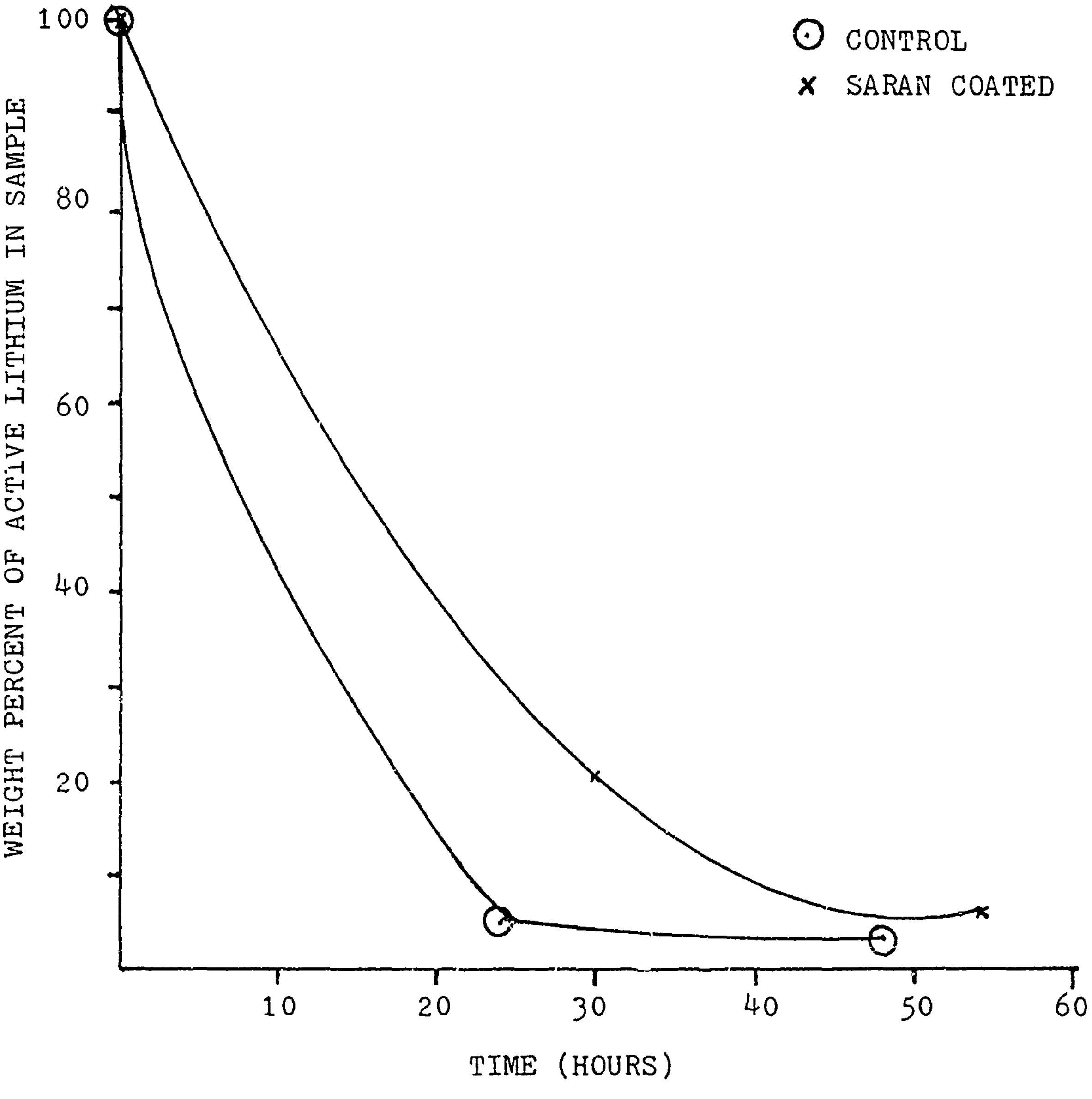


Figure 6. Effects of Saran Coating on Run 2-1 Reported as Active/Payload*100% at 55°C and 9% R.H.

TABLE 8. REPLICATED ANALYTICAL DETERMINATIONS FOR SAMPLE 2-12 HAVING A THEORETICAL PAYLOAD OF 34.0 PERCENT

	Weight Percent of Lithium	
	Elemental*	Total**
	26.2	31.5
	24.4	31.2
	31.3	31.2
Mean	27.3	31.4
Standard Deviation	3.6	0.14

*Determined by gas evolution method

**Determined using ion chromatography

volume ratio and consequently a thinner outer coating on the lithium particles close to the microsphere wall. Thus, a low elemental lithium content may be due to a large number of small microspheres in the sample.

Until precision among elemental lithium contents is improved, statistical significance between various experimental runs cannot be determined.

CONCLUSIONS AND RECOMMENDATIONS

Micronized lithium metal can be encapsulated to increase shelf-life and stability of elemental lithium. Under this program, SwRI developed non-reactive protective coatings, experimental procedures, and analytical methods for the production of lithium microspheres and submitted three one-pound samples and one ten-pound sample of lithium microspheres for evaluation.

With standard operating procedures developed and experience gained on this program, additional quantities of lithium microspheres can be produced at a lower cost per pound. It is recommended that future programs include analytical methods development for increased reproducibility of elemental lithium determinations. Furthermore, the second coating approach using Saran or some other protective barrier and optimization of the payload and matrix should be pursued in future programs to improve shelf-life characteristics.

APPENDIX A

STANDARD OPERATING PROCEDURES

METHOD TO PREPARE MICRONIZED LITHIUM METAL IN MATRIX DISPERSION TO MAKE MICROSPHERES VIA THE ELECTRICALLY-POWERED DISK

Safety Precautions

1. Cleaning, weighing, amd mixing operations shall be performed in an argon atmosphere, both to prevent degradation of the lithium by reaction with oxygen, nitrogen, or water vapor and as a safety measure to protect project personnel.

2. Microencapsulation process shall be performed in a carbon dioxide atmosphere.

3. Handle lithium with rubber or plastic gloves; avoid bodily contact with micronized lithium metal. Safety goggles and flame-proof clothing are recommended.

4. Burning lithium is to be extinguished by spraying a graphite powder fire extinguisher in the air above the burning lithium so that the powder gently settles on top of the flame and smothers it. Small fires may be extinguished by sprinkling dry lithium chloride on top of lithium flame.

5. DO NOT use water, sand, carbon-tetrachloride, carbon dioxide, or acid-soda fire extinguishers.

6. Avoid exposure of lithium to water and air.

7. Never work with lithium alone. Always have at least two people working together.

8. Before opening a sealed package of micronized lithium metal inside a glove box, the oxygen concentration as monitored by the GC Industries Oxygen Monitor/Alarm, Model GC 501 should be less than 1%.

9. Before doing any work in a glove box, the pressure inside the glove box as monitored by the Dwyer Instruments Photohelic Pressure Switch/Gage should be positive.

10. In the event of an accident, the following items have been provided to minimize the severity of the accident:

    - Telephone in the adjacent room to the encapsulation area is to be used to dial 2222 in the event of a severe accident requiring medical or fire protection assistance.

    - Aluminum foil blow-out sections have been added to the glove boxes so that pressures developed inside the enclosed area would be minimal in the event of an accident and so the area of severe danger (exploding hydrogen gas or lithium metal fire) would be known, would be away from personnel work areas and would be in an easy access place for fighting a fire.

- Dry lithium chloride in 500-gram plastic containers are near the work areas. In the event of a small lithium fire, sprinkle the dry lithium chloride on top of the burning area to extinguish the fire.

- Two graphite/lithium chloride fire extinguishers are in the work area to fight large fires.

- One safety fire blanket is in the work area. In the event that a person's clothing catches on fire, wrap the blanket around the person to extinguish the fire then call extension 2222 for immediate assistance.

First-Aid Treatment

Lithium burns on the skin are of the same nature as caustic burns and require immediate first-aid treatment. If any particles of lithium adhere to the skin, it should be quickly brushed off and must be copiously washed with water for 15 minutes. After washing, the affected area should be covered with sterile dressing. Call extension 2222 for immediate medical assistance.

Enclosure for Working with Micronized Lithium Metal

A. Preparation Area Glove Box, Cleaning Operations

1. The cleaning operation to obtain dry micronized lithium metal from the mineral oil lithium dispersion is two steps.

2. The lithium metal dispersion, as received from Lithium Corporation of America is a 30% by weight micronized lithium metal dispersed in mineral oil and is stored in a one-gallon sealed can. After several days of storage, the dispersion in the can is inhomogeneous. Since the lithium has a much lower density than the mineral oil, the lithium floats on the top of the mineral oil. The consistency of the dispersion is thus a thick slurry (almost the consistency of a thick paste) on top and free-flowing liquid on the bottom. Do not open the can when the contents are in this state.

3. Put the sealed one-gallon can containing the lithium metal dispersion on a paint shaker for several hours. This will result in a homogeneous free-flowing lithium dispersion.

4. Place the one-gallon can immediately after being shaken in the Preparation Area Glove Box. Add the following items also to the glove box:

   - manual can opener
   - scoop
   - six empty 32-ounce wide-mouthed plastic-coated safety bottles with caps
   - Parafilm M
   - scissors
   - spatula

- o three wash bottles containing n-pentane
- o one 32-ounce wide-mouthed plastic-coated safety bottle with cap filled with mineral oil
- o several hand towels.

5. Seal the glove box.

6. Purge the glove box with argon. Be sure that all jars and wash bottles have lids removed so that air and water vapor are not sealed inside these containers the contents of which could react with the lithium metal.

7. Once the oxygen level is below 1%, open the one-gallon can containing lithium metal dispersion with the manual can opener.

8. Scoop the lithium metal dispersion from the can into the empty wide-mouthed plastic-coated safety jars. Put lids on jars as they are filled.

9. When most of the lithium metal dispersion is out of the can, carefully bend the can to form a spout. Pour the remaining dispersion into the wide-mouthed plastic-coated safety jars.

10. Rinse the metal can with pentane and pour mixture into plastic-coated safety jars.

11. Use spatula to assist removal of all of the dispersion from the metal can.

12. Seal all plastic-coated safety jars with their lids, then wrap lips with Parafilm M (scissors will be required to cut the Parafilm M to desired lengths).

13. Wash down all surfaces containing spilled lithium dispersion with towels and mineral oil.

14. Place contaminated rags in empty metal can and cover with mineral oil.

15. Turn off argon supply. Open glove box. Remove contents.

16. Store plastic-coated jars containing lithium metal dispersion in metal drum packed with vermiculite.

17. Carefully treat the soiled rags with small amounts of isopropanol to slowly react the lithium in a controlled manner.

18. The second step is to clean the dispersion that is stored in the plastic-coated wide-mouthed jars.

19. Add 2 plastic-coated wide-mouthed jars filled with lithium metal dispersion, a spatula, 5 empty plastic-coated wide-mouthed jars, 3 wash bottles of pentane, 2 plastic-coated wide-mouthed jars filled with pentane, Parafilm M, scissors, filter paper, filter assembly, and vacuum line to glove box.

20. Purge glove box with argon. Do not begin operations until O_2 is below 1%.

21. Add 100 mL of lithium dispersion to filter assembly. Apply suction to filter.

22. Using a plastic wash bottle, rinse lithium dispersion with dry pentane.

23. Repeat rinses until lithium powder is free of mineral oil.

24. Turn off suction when residual pentane is removed from the lithium powder.

25. Put pentane/mineral oil liquid into empty plastic-coated wide-mouthed jars.

26. Allow lithium powder on filter to dry.

27. Transfer dry lithium powder to empty plastic-coated wide-mouthed jars.

28. Repeat steps 22 through 27 until all lithium metal dispersion is clean.

29. Clean up as outlined in Steps 12 through 17.

B. <u>Microencapsulation Area</u>

1. Enclosure contains the electric disk.

2. Enclosure shall be under a carbon dioxide atmosphere during microencapsulation process.

3. Product collection in this enclosure is done under normal atmospheric conditions.

4. The enclosure was framed with 2 x 4's and 2 x 6's and lined with 1/2-inch gypsum board.

C. <u>General</u>

1. The room housing these facilities is located in SwRI Building 96 and is rated for hydrocarbon usage.

2. The room will be well ventilated to purge any pentane vapors and residual argon and carbon dioxide.

3. The room has water sprinklers to protect against a large fire initiated by lithium metal. A fire of this size would consume all lithium and the constructed enclosures.

Preparation of Lithium/Matrix Material Emulsion (Perform in an Argon Atmosphere)

1. Add preweighed sealed containers of matrix material and micronized lithium metal. Seal glove box. Purge with argon to less than 1% oxygen.

2. Transfer matrix material to feed reservoir. Melt matrix material.

3. Mix lithium powder into melted matrix material. Stir for one hour.

4. Emulsion is ready for preparation of microspheres.

Preparation of Microspheres

1. Purge Encapsulation Area with liquid carbon dioxide.

2. Once feed tube and disk have been heated, begin spinning disk.

3. Open feed system ball valve to transfer emulsion from reservoir to disk.

4. Microspheres are formed by the disk and solidify as they fall to the collection area in a carbon dioxide atmosphere.

5. Close ball valve when feed reservoir is empty.

6. Turn off heat and spinning disk.

7. Open enclosure and purge out carbon dioxide.

8. Collect the microspheres using rubber gloves.

Analytical Procedures

1. Evaluate sample for particle size distribution.

2. Put one small sample of microspheres (approximately 1 gram) into each constant temperature and relative humidity chamber for aging study.

3. Give a small sample of microspheres (approximately 100 mg) to analytical lab to determine elemental lithium and total lithium ion concentrations.

4. Package remaining sample under argon for shipment in plastic-coated, shatterproof, safety jars.

APPENDIX B

RAW MATERIAL PRODUCT SPECIFICATION SHEETS

Lithium Metal Dispersion

Li metal in mineral oil
Light brown liquid

CAS Registry No. 7439-93-2

LITHCO
Lithium Corporation of America
449 North Cox Road
Gastonia, North Carolina 28052
(704) 867-8371
Telex 57-5253

Composition

	Typical Weight Percent
Lithium metal, high purity	30
Mineral oil	69
Oleic acid (dispersing agent)	1

Physical Analysis

Particle size

100%	less than 50 μm
90%	less than 50 μm, greater than 10 μm

Toxicity/Safety Data

Lithium metal, regardless of form, is a highly reactive substance, particularly at elevated temperatures. The main hazard is its reaction with moisture to form hydrogen and caustic lithium hydroxide. Care should be taken to prevent contact with the eyes and skin. Affected areas should be flushed with copious amounts of water and treated for caustic burns. If the eyes are involved, seek prompt medical attention.

Handling/Storage/Disposal

The precautions for handling lithium metal dispersions are similar to those used in handling any alkali metal. Lithium metal dispersions should be handled only by persons wearing protective equipment, including safety goggles, rubber gloves and apron. After opening the original container, lithium dispersions should be stored in a container with a tight pressure lid to avoid decomposition by atmospheric nitrogen and moisture. The dispersions may settle some during storage, but uniformity can be restored by stirring, perhaps with a gentle heating over a sand bath. Spilled dispersion should be scraped up immediately. The residue should be flushed with mineral oil and cautiously wiped up with a rag wet with mineral oil. Do not use a dry cloth or one wet with water. Destroy waste dispersion by burning in a safe, open area. Avoid breathing the fumes from waste fires, they are caustic and highly irritating.

Other Comments

Laboratory apparatus may be cleaned by flushing with a 15% solution of isopropanol in light mineral oil or kerosene. Larger containers may be cleaned by flushing with dry steam or burning the residue. Industrial safety practices for alkali metals should be followed, including the use of a safe decontamination area.

Lithium metal powder can be extracted from the mineral oil matrix by dissolving the matrix in a volatile hydrocarbon solvent (e.g., pentane or hexane), filtering under argon, and vacuum drying to remove the solvent.

Lithium Metal Dispersion

Li metal in mineral oil

Shipping Containers

Small quantities of lithium metal dispersion are packed in hermetically sealed cans and overpacked for shipment in DOT-specified wooden boxes or steel drums. Larger quantities are packaged in bulk in DOT-specified steel pails or drums.

Shipping Limitations

Via	Regulations
Postal Service	Not acceptable
UPS	Not acceptable
Air	Limit of 25 lb (11.25 kg) per container on cargo aircraft only
Water	Permitted on cargo vessel only
Rail	Authorized amounts in DOT-specified packaging (Not permitted on passenger rail car)
Truck	Authorized amounts in DOT-specified packaging

Shipments of lithium metal are required by the DOT to have container labels specifying "Flammable Solid" and "Dangerous When Wet." Lithium metal dispersion has been designated UN No. 1415. Shipments by water are IMCO Class 4.3.

Lithium Corporation of America is a subsidiary of Gulf Resources & Chemical Corporation

LITHIUM CORPORATION OF AMERICA
A SUBSIDIARY OF GULF RESOURCES & CHEMICAL CORPORATION
BESSEMER CITY, NORTH CAROLINA 28016 • (704) 629-2282

Date: March 28, 1985

CERTIFICATE OF ANALYSIS

Customer: Southwest Research Institute
P.O. Box 28510
6220 Culebra Road
San Antonio, TX 78284

Customer Order No: 58137 Martha

L.C.A. Order No: 035643

Product: Lithium Metal Dispersion

Amount: 10 Pounds

Date Shipped: 3/28/85

ANALYSIS

Typical:

% Lithium	30
Na	.02
Mineral Oil	69
Oleic Acid	1

Stanley M. Joyner, Quality Services

LITHIUM CORPORATION OF AMERICA
A SUBSIDIARY OF GULF RESOURCES & CHEMICAL CORPORATION

ORIGINATOR:
DISTRIBUTION:

	THIS	REPLACES
FILE:	1500-491	
DATE:	11/19/80	4/2/79
PAGE:	6 OF 6	OF

MATERIAL SAFETY DATA SHEET

SECTION I

CAS REGISTRY NO: 7439-93-2

MANUFACTURER'S NAME LITHIUM CORPORATION OF AMERICA	EMERGENCY TELEPHONE NO. 704 - 629 - 2282
ADDRESS (Number, Street, City, State, and ZIP Code) Highway 161, BESSEMER CITY, N.C. 28016	
CHEMICAL NAME AND SYNONYMS Lithium Metal	TRADE NAME AND SYNONYMS Lithium Metal Dispersion
CHEMICAL FAMILY Alkali Metal	FORMULA Li

SECTION II HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS		%	TLV (Units)	ALLOYS AND METALLIC COATINGS		%	TLV (Units)
PIGMENTS	N/A			BASE METAL	Lithium	30	
CATALYST	"			ALLOYS	"		
MINERAL OIL		69		METALLIC COATINGS	"		
OLEIC ACID		1		FILLER METAL PLUS COATING OR CORE FLUX	"		

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	TLV (Units)

SECTION III PHYSICAL DATA

BOILING POINT (°F.) (°C)	1317.0	SPECIFIC GRAVITY ($H_2O=1$)	g/ml	0.534
VAPOR PRESSURE (mm Hg.) 20°C)	nil	PERCENT VOLATILE BY VOLUME (%)		
MELTING POINT (°C)	180.5°C	EVAPORATION RATE (________ =1)		
SOLUBILITY IN WATER	Reacts violently			
APPEARANCE AND ODOR	A light grey colored metal slurry in oil; odorless			

SECTION IV FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used) (mineral oil) 177°C (coc)	FLAMMABLE LIMITS	Lel	Uel

EXTINGUISHING MEDIA Dry lithium chloride or graphite powder.

SPECIAL FIRE FIGHTING PROCEDURES Keep Li metal fire confined as much as possible to a small area. Cover with dry lithium chloride. Water, moist sand, carbon dioxide or acid soda ash extinguisher should not be used.

UNUSUAL FIRE AND EXPLOSION HAZARDS

Essentially same as Form LSB-005-4 May 1969 - Form Approved OMB No. 44-R1387 - OSHA Form 20

SECTION V HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE N/A - reactive alkali metal

EFFECTS OF OVEREXPOSURE Contact with the skin or the eyes result in caustic burn and irritation. Molten lithium causes severe burns.

EMERGENCY AND FIRST AID PROCEDURES Skin - flush thoroughly with water; consult a physician.

Eye contact - Flush with copious amounts of water for at least 20 min.; then consult an ophthalmologist.

SECTION VI REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	

INCOMPATABILITY (Materials to avoid) Water and alcohols

HAZARDOUS DECOMPOSITION PRODUCTS Reacts with water to liberate hydrogen and caustic lithium hydroxide.

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED Wear coveralls and rubber gloves, safety glasses and face shield. Then with dry broom, sweep up into shovel and return to steel container; label or tag. Keep away from moisture and water.

WASTE DISPOSAL METHOD Dispose according to local or state EPA waste disposal regulations.

SECTION VIII SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type) Normally not needed.

VENTILATION	LOCAL EXHAUST	SPECIAL
	MECHANICAL (General)	OTHER

PROTECTIVE GLOVES Plastic or rubber gloves	EYE PROTECTION Safety glasses and face shield

OTHER PROTECTIVE EQUIPMENT Plastic or rubber apron; fire retardant coverall

SECTION IX SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING Store at room temperature in a dry place and avoid exposure to water.

OTHER PRECAUTIONS Cans of lithium dispersion should be rotated end to end twice a month.

No guaranty is made as to the accuracy of any data or statements contained herein. While this material is furnished in good faith, no warranty expressed or implied, of merchantability, completeness, fitness or otherwise is made. This material is offered only for your consideration, investigation and verification, and Lithium Corporation of America disclaims any liability incurred from the use thereof and shall not in any event, be liable for any special, incidental or consequential damages arising from such use. This information is not intended to be all inclusive and the manner and conditions of use and handling of the material involved may involve other or additional considerations. It should not be construed as a recommendation of any specific use.

Boler Petroleum Company
85 Old Eagle School Road, P.O. Box 384
Wayne, Pennsylvania 19087 U.S.A.

International Waxes Limited
50 Salome Drive, Agincourt
Ontario, Canada M1S 2A8

Malcolm Nicol & Co. Inc.
Page Avenue and Orient Way
Lyndhurst, New Jersey 07071

The INTERNATIONAL Group

technical information sheet

Boler Petroleum Company

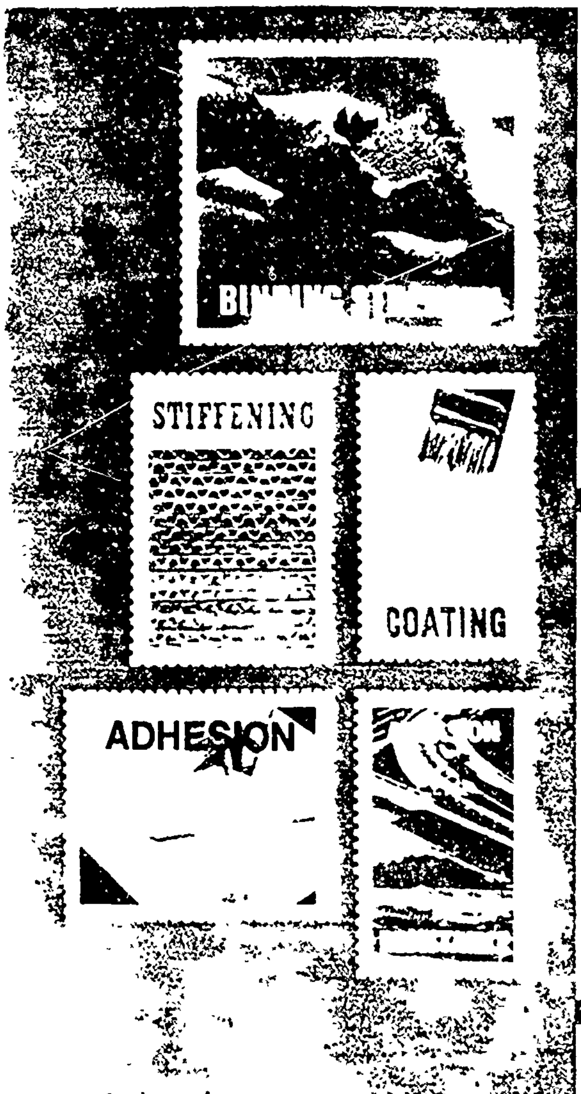
1426 FULLY REFINED PARAFFIN WAX

SPECIFICATIONS:

Melting Point (AMP)	155/160°F
Melting Point (ASTM D-87)	152/157°F
Oil Content (ASTM D-721)	0.9% Maximum
Color, Saybolt (ASTM D-156)	+28 Minimum
Penetration (ASTM D-1321) @ 77°F	12 Typical
" " @ 90°F	20 Typical
" " @ 100°F	28 Typical
Saybolt Viscosity @ 210°F	49.5 Typical

FDA STATUS:

Boler 1426 Fully Refined Paraffin Wax meets the FDA requirements and may be safely used in or on food under the provisions of Paragraph 172.886. It may also be safely used as a component of nonfood articles in contact with food under the provisions of Paragraph 178.3710.



PICCO* resin plasticizers

Soft polymers used for plasticizing, softening, tackifying, and extending. Excellent for adhesive use.

PICCOUMARON* resins

Coumarone-indene type resins which are highly aromatic, with excellent compatibility with most materials used in rubber compounding, co[illegible] and [illegible]

PICCOLYTE* Alpha resins

A series of resins made from alpha pinene, used in hot melt adhesives, [illegible] adhesives, water proofing [illegible], and [illegible]

Dipentene PICCOLYTE* resins

A series of [illegible] tackifying [illegible]

PICCO* resin plasticizers	PICCOVAR AP-10	PICCOVAR AP-25	PICCOVAR AP-33	PICCOVAR L-30	PICCOVAR L-60	DIPOLYMER OIL M	PICCOCIZER 30 M
Color, Coal Tar Scale	2½	2½	3	1½	1½	8 -*	8 -*
Softening Point, °C	10	32	36	31	57	—	—
Flash Point, COC, °F	290	430	445	455	475	190	192
Fire Point, COC, °F	395	505	500	515	560	220	222
Acid No., Max.	1.0	1.0	1.0	1.0	1.0	—	—
Saponification No., Max.	1.0	1.0	1.0	1.0	1.0	—	—
Bromine Number	3.0	3.1	3.4	1.3	1.5	—	—
Iodine Number	31	32	32	40	43	—	—
Specific Gravity	1.01	1.01	1.01	1.04	1.04	1.01	1.04
Pounds per Gallon	8.41	8.41	8.41	8.66	8.66	8.37	8.66
Melt Viscosity, °C						*ASTM COLOR	
1 poise	85	108	112	93	129	—	—
10 poises	55	78	80	66	97	—	—
100 poises	40	60	57	49	77	—	—

PICCOUMARON* resins	10	25	422-R	*410-L **410/450-L***	*410-HL **410/450-HL***	*410-EHL **410-EH/450 EHL***
Color, Coal Tar Scale	1 — —	1 — —	1 — —	1½* 1** 1½***	½* 1** 1½***	½* 1** 1½***
Softening Point, °C	15	37	76	100	110	120
Flash Point, COC, °F	370	390	425	500	520	540
Fire Point, COC, °F	415	435	485	560	580	600
Acid No., Max.	1.0	1.0	1.0	1.0	1.0	1.0
Saponification No., Max	2.0	2.0	2.0	2.0	2.0	2.0
Iodine Number	46	45	54	55	52	52.0
Specific Gravity	1.04	1.05	1.12	1.10	1.10	1.12
Melt Viscosity, °C						
1 poise	85	112	156	185	195	206
10 poises	58	83	131	153	165	175
100 Poises	41	66	113	130	145	154

NOTE All Values Are Nominal

PICCOLYTE* Alpha resins	A-10	A-25	A-40	A-55	A-70	A-85	A-100	A-115	A-125	A-135
Color, Gardner	4	4	4	5	6	6	6	6	5	5
Softening Point, °C	10	25	40	55	70	85	100	115	125	135
Specific Gravity @ 25°C.	0.93	0.94	0.94	0.95	0.96	0.96	0.97	0.97	0.97	0.97
Bromine Number	17	19	23	23	23	28	28	31	31	31
Iodine Number	35	36	44	44	44	56	56	62	62	62
Flash Point, °F.	445	440	420	440	430	430	420	420	420	450
Fire Point, °F.	480	480	480	480	480	480	480	480	495	510
Saponification Number	1	1	1	1	1	1	1	1	1	1
Saponification Number	1	1	1	1	1	1	1	1	1	1
Melt Viscosity, °C										
1 poise	100	110	125	150	155	170	185	200	210	220
10 poises	60	80	90	105	125	133	150	160	175	185
100 poises	40	60	70	85	100	110	130	140	155	160

Dipentene PICCOLYTE* resins	115	135
Color, Gardner	3	4
Softening Point, °C	115	135
Specific Gravity @ 25°C	0.98	0.975
Bromine Number	28	27
Iodine Number	112	116
Flash Point, °F	460	485
Fire Point, °F	530	555
Acid Number	1	1
Saponification Number	1	1
Melt Viscosity, °C		
1 poise	211	232
10 poises	174	197
100 poises	147	170

PPN-066-C

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HERCULES
INCORPORATED
ORGANICS DEPARTMENT
PICCO®
RESINS
120 State Street, Clairton Pennsylvania 15025

Designed by Reeds and Farris

Printed in U S A /BNJR

Epolene® Waxes

Low Molecular Weight Polyethylene Resins for Industrial Applications

EASTMAN CHEMICAL PRODUCTS, INC. Kingsport, Tennessee 37662

Emulsifiable Waxes

Epolene E-10

Specifically developed for water-emulsion floor polishes. Epolene E-10 wax imparts excellent slip resistance to polish films, together with outstanding toughness, durability and good wear properties. Emulsions of Epolene E-10 also contribute high gloss, hardness and good resistance to scuff and dirt pickup. These properties are often apparent at low wax concentrations, however, they are best observed where Epolene E-10 wax represents 20% or more of the total solids in the polish.

Emulsions of Epolene E-10 may be used as finishing agents for cotton and rayon fabrics and as textile softeners in conjunction with wash-and-wear finishing waxes.

Emulsions prepared with Epolene E-10 may be used as lubricants in clay coatings for paper to reduce dusting during calendering.

Epolene E-11

Intermediate, low-density emulsifiable wax with a lower molecular weight than Epolene E-10 and, thus, a lower melt viscosity.

Epolene E-11 wax is useful in emulsion floor polishes where good slip resistance is required in formulations containing less than 20% emulsifiable waxes.

Emulsions of Epolene E-11 also find utility as textile finishing agents. A primary benefit of Epolene E-11 in this application is its ease of emulsification.

Epolene E-12 and Epolene E-45

Emulsifiable waxes specifically designed for use as textile lubricants. Epolene E-12 and Epolene E-45 waxes have higher densities than the other E-type waxes. This produces greater hardness and higher softening points in these products.

Nonionic and cationic emulsions of the high density Epolene waxes are especially effective for use with wash-and-wear finishing resins. These emulsions impart better tensile strength, abrasion resistance, sewability and hand to wash-and-wear fabrics without reducing crease-angle recovery. They also impart a soft hand when used as softeners for synthetic fabrics and they improve the snag resistance of knit goods.

Floor polishes formulated with Epolene E-12 or Epolene E-45 exhibit considerable hardness and a corresponding reduction in slip resistance. Best results are obtained when the high density Epolene waxes are used in combination with softer synthetic waxes and natural waxes in mixed wax emulsions for highly buffable polishes.

The high density and softening point of Epolene E-12 and Epolene E-45 waxes make them particularly attractive for use in emulsions for coating citrus fruit. These properties contribute to the hardness fast tack-free dry time and gloss of the emulsion coatings.

Epolene E-14 and Epolene E-15

Emulsifiable waxes with low densities and softening points. These properties contribute greatly to their versatility and ease of emulsification by the water-to-wax, wax-to-water or pressure emulsification methods. Epolene E-14 wax imparts excellent slip resistance to floor polish films. Best results are obtained when Epolene E-14 is used in concentrations of 20% or less, or in polishes containing natural and synthetic waxes. Epolene E-15 is the softest of the emulsifiable waxes and is used at low concentrations in mixed wax emulsions and high polymer floor polishes to improve slip resistance.

Epolene E-14 and N-14 (powdered form) are useful as lubricants in processing rigid and flexible polyvinyl chloride.

Epolene E-43

A chemically modified polyolefin with the greatest hardness and highest melting point of all the emulsifiable Epolene waxes. Pressure equipment is essential for the emulsification of this material. Contrary to what might be expected from such a hard wax, Epolene E-43 imparts outstanding slip resistance to floor polishes.

Nonemulsifiable Waxes

Epolene N-10

A nonemulsifiable wax of medium density and a relatively low melting point. Epolene N-10 wax is easily blended with natural or synthetic waxes to gain improved tensile strength abrasion resistance and adhesion to fibrous substrates. For paper coating applications such as folding cartons, Epolene N-10 not only increases wax mileage but also provides a glossy flexible, scuff-resistant finish. Epolene N-10 also can be used in printing inks to improve resistance to scuffing and rub-off.

Epolene N-11, Epolene N-14, and Epolene N-34

These three Epolene waxes are all lower in molecular weight and density than Epolene N-10. Their applications are similar to those for Epolene N-10, but they offer advantages where wax modifiers with low viscosities and cloud points are needed.

Epolene N-11 or N-34 may be used as a solid lubricant in the manufacture of corrugated board. These waxes provide performance superior to oil-mist systems in lubricating corrugated medium.

Epolene N-12 and Epolene N-45

These high density, high melting point, hard polyethylene waxes are used to raise the blocking temperature of wax blends and to upgrade low melting paraffins. Also, they are used as mold release additives in rubber molding and as extrusion aids for vinyl processing.

Epolene N-15

A low density, low viscosity polypropylene resin with an unusually high melting point and penetration hardness. These features suggest its use as a modifier for petroleum waxes to increase blocking, scuff and abrasion resistance and as a compounding resin for hot melt adhesives.

Epolene C-10

Low density wax especially designed for use in hot melt coatings for coated papers and packaging materials. Coatings produced with Epolene C-10 wax or blends containing Epolene C-10 exhibit high gloss, low moisture vapor transmission rates, good grease resistance and good heat sealability. However, Epolene C-10 is not limited to use in hot melt coatings; it also can be used as a paraffin modifier in slush and cast molding, in hot melt adhesives, and in rigid and flexible vinyl compounds.

Epolene C-13, Epolene C-14, and Epolene C-17

Designed for use in combination with other Epolene waxes or in blends containing lower molecular weight materials. As petroleum wax modifiers these three Epolene waxes increase blend viscosity which is important for controlling penetration into paper substrates. Blends of these Epolene waxes with paraffin offer improved grease resistance, higher blocking temperatures, better scuff resistance and improved gloss. Other major uses are as additives for inks and as compounding resins for hot melt adhesives.

Epolene C-15

As an additive for folding cartons Epolene C-15 wax imparts high gloss, good gloss retention and improved hold-out. Easily modified with low cost resins Epolene C-15 is useful in formulating hot melt adhesives and as a candle additive to provide gloss, sheen, opacity and good mold release.

Epolene C-16

As a hot melt coating for paper, Epolene C-16 wax provides a glossy barrier coating which may be readily heat sealed to most paper products, metal foils and polyolefin films. In petroleum wax coatings, Epolene C-16 provides good gloss retention, scuff resistance and, in certain formulations, heat sealability. As an additive in wax-copolymer coatings Epolene C-16 can provide increased hot tack, scuff resistance and gloss stabilization.

TYPICAL PROPERTIES* OF EPOLENE® WAXES

	Emulsifiable Types						
	E-10	E-11	E-12	E-14	E-15	E-43	E-45
Ring and Ball Softening Point, °C	106	106	107	104	100	157	114
Penetration Hardness, 100g/5 sec/25°C, tenths of mm	3	3	1	4	7	0-1	1
Density, 25°C	0.942	0.941	0.955	0.939	0.925	0.934	0.964
Acid Number	15	15	16	16	16	47	16
Brookfield Viscosity, cp[a]							
125°C (257°F)	1200	450	390	320	520	b	350
150°C (302°F)	800	200	180	175	390	b	160
190°C (374°F)	225	65	60	50	105	370	55
Color, Gardner Scale	2	2	1	2	2	11	1
Molecular Weight, approximate	3,000	2,200	2,300	1,800	3,400	4,500	2,100

[a] Spindle #3; 6 rpm [b] Solid at this temperature

AVAILABILITY OF POWDERED WAXES

Most N- and C-type Epolene waxes are available in powdered form. For specific information about powdered Epolene waxes, contact your Eastman representative.

*Reported for information only. These figures are average values for typical production material and should not be construed as specifications.

TYPICAL PROPERTIES* OF EPOLENE® WAXES

	Nonemulsifiable Types												
	N-10	N-11	N-12	N-14	N-15	N-34	N-45	C-10	C-13	C-14	C-15	C-16	C-17
Ring and Ball Softening Point, °C	111	108	113	106	166	103	118	104	110	>133	102	106	133
Penetration Hardness, 100g/5 sec/25°C, tenths of mm	2	2	1	3	0.6	4.6	0.1	3	3	2	4	3	2
Density, 25°C, g/cc	0.925	0.921	0.938	0.920	0.860	0.910	0.947	0.906	0.913	0.918	0.906	0.908	0.917
Acid Number	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	5[a]	<0.05
Brookfield Viscosity, cp[b]													
125°C (257°F)	1800	480	430	230	e	660	450	12,000	3×10^{5}[c]	e	7,500	14,000	e
150°C (302°F)	840	350	115	80	e	375	330	9,400	85,000	1×10^{7}[c]	4,300	12,000	9×10^{5}[c]
190°C (374°F)	425	95	75	45	3,750	145	90	4,000	4×10^{4}[c]	5×10^{6}[c]	1,100	5,000	4×10^{5}[c]
Melt Index, 190°C	—	—	—	—	2,200	—	—	2,250	200	1.6	4,200	1,700	20
Color, Gardner Scale	1	1	1	1	1	1	1	1	1	1	1	1	1
Molecular Weight[c]	3,000	2,200	2,300	1,800	14,000	2,900	2,100	8,000	12,000	23,000	4,000	8,000	19,000
Cloud Point,[d] °C	85	79	87	77	104	69	97	77	81	84	75	78	81

[a] Saponification number [b] Spindle #3; 6 rpm [c] Approximate [d] 2% in 130°F paraffin [e] Solid at this temperature

Applications

Adhesives, hot melt	N-15, N-34, All C-types
Cable filler	N-12, N-45
Candles	N-11, N-34, C-10, C-15
Carpet backing	C-10, C-13, C-14, C-16, C-17
Citrus fruit coatings‡	E-10, E-12, E-45
Coils and condensers, potting compounds for	C-10, C-13, C-14, C-15, C-17
Color concentrates	N-11, N-15, C-10, C-15
Corrugated board, coating for	All C-types
Corrugated board, surface lubricant	E-10, N-11, N-34
Crayons	N-14, N-45, C-15
Extrusion aids	E-14, N-12, N-14, N-45
Fibre drums, coated paper for	C-10, C-13, C-15
Folding cartons, modified wax coating for	N-10, N-11, N-12, N-14, N-34; All C-types
Furniture polish	E-10, E-11, E-14
Glass bottles, scuff-resistant coating for	All E-types
Mold release agent for urethane foam	All E-types, C-16
Packaging materials, lamination of	C-10, C-13, C-15, C-16, C-17
Paint and varnish compounding	N-11, N-14, N-34, N-45, E-10
Paper, clay coating lubricant	E-10, E-12, E-14
Paper coatings, hot melt	All N- and C-types except N-15
Paper coatings, emulsion	All E-types
Paper, carbon	All N-types except N-15
Polishes, automotive	E-10, E-12, E-45
Polishes, emulsion floor	All E-types
Polishes, paste	All N-types except N-15
Printing inks	All E- and N-types except N-15, C-10, C-13
Rubber compounding	N-10, N-11, N-14, N-34, N-45, C-10, C-15
Slush molding	N-34, C-10, C-13, C-15
Spreader-sticker, agricultural spray	All E-types
Textile finishes	All E-types
Vinyl compounding	E-14, N-14, N-34, N-45, C-10, C-16
Wax modification, general	All C- and N-types

‡Within the United States, under U. S. Food Additive Regulation 21 CFR 121.1142, it is lawful to use the emulsifiable Epolene waxes, except E-43, as components of coatings for fresh avocados, bananas, beets, coconuts, eggplants, garlics, grapefruits, lemons, limes, mangos, muskmelons, onions, oranges, papayas, peas (in pods), pineapples, plantains, pumpkins, rutabagas, squash (acorn), sweet potatoes, tangerines, turnips, watermelons, Brazil nuts, chestnuts, filberts, hazelnuts, pecans, walnuts (all nuts in shells). In other countries, the appropriate government regulatory agencies should be contacted.

SAFETY PRECAUTIONS

Material Safety Data Sheets providing handling, storing, and other precautions are available for the Eastman products mentioned in this publication. Users of these products should review the applicable MSDS before handling any of these products. Write, or call our toll free number.

FOR FURTHER INFORMATION

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Kingsport, Tennessee 37662

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APPENDIX C

ANALYTICAL METHOD FOR DETERMINATION OF ELEMENTAL LITHIUM

DETERMINATION OF ELEMENTAL LITHIUM CONTENT IN MICROSPHERES

1. Weigh about 100 mg of microspheres into the flask. Record the exact weight to the nearest 0.1 mg.
2. Add 25 mL of dry mineral oil to the flask.
3. Connect the flask to the gas buret.
4. Place the dropping funnel containing 10 mL of H_2O on the flask.
5. Purge the apparatus with argon for 2-3 minutes.
6. Place the oil bath on the flask and heat the magnetically stirred flask until the microspheres melt and the lithium disperses in the mineral oil.
7. Cool the mixture to room temperature.
8. Zero the gas buret and position the stopcock to connect the flask to the buret.
9. Add H_2O dropwise to the stirred flask. As H_2 is evolved, maintain the gas buret at approximately atmospheric pressure.
10. When gas evolution stops, add the remaining H_2O in the dropping funnel, wait 2-3 minutes, and adjust the gas buret exactly to atmospheric pressure using the leveling bulb and the small water manometer.
11. Read the volume on the gas buret to the nearest 0.1 cm^3. Record the volume.
12. Read the thermometer and record the temperature.
13. Read the barometer and record atmospheric pressure.

<u>**Calculations**</u>

1. Determine the vapor pressure of water at the recorded temperature from the appropriate table.
2. Subtract the vapor pressure of water from the recorded atmospheric pressure.

3. Calculate the millimoles of hydrogen gas evolved using the following equation.

$$N_{H_2} = \frac{PV}{RT}$$

where N_{H_2} = mmoles of H_2

P = atmospheric pressure corrected for H_2O vapor pressure, atm

V = volume of hydrogen gas, mL

R = gas constant, [0.08206 (mL·atm)/(°K·mmole)

T = temperature, °K.

4. Calculate the mg of Li

$$2 \times N_{H_2} \times 6.940 = \quad \text{mg Li}$$

5. Calculate payload (elemental lithium)

$$\frac{\text{mg Li}}{\text{mg microspheres}} \times 100 = \quad \text{\% elemental lithium payload.}$$

CALCULATION OF ELEMENTAL LITHIUM IN MICROSPHERES

Name: Date:

Sample Number: Project Number:

Aging Conditions (if any):

1. Weight of sample ____________ mg capsules
2. Volume reading on gas buret _________ mL
3. Thermometer reading _____°C + 273.15 = __________ °K
4. Barometer reading _______ in Hg x 25.4 = ______ mm Hg
5. Vapor pressure of water at recorded temperature _______ mm Hg
6. Corrected pressure (subtract vapor pressure of water from recorded atmospheric pressure) _____ mm Hg ÷ 760 = _________ atm
7. Millimoles of hydrogen evolved (the product of volume reading on gas buret and corrected pressure divided by the product of the gas constant and temperature) ____ mL x ____ atm / 0.08206 x _______ °K = ______ mmoles H_2
8. Milligrams of elemental lithium _____ mmoles H_2 x 13.88 = _______ mg Li
9. Sample payload (elemental lithium) _____ mg Li / _____ mg microspheres x 100% = _____ %

APPENDIX D

MATERIAL SAFETY DATA SHEET FOR LITHIUM METAL AND LITHIUM CORPORATION OF AMERICA'S PRODUCT BULLETIN DESCRIBING HANDLING, STORAGE, AND SAFETY PRECAUTIONS

LITHIUM CORPORATION OF AMERICA
A SUBSIDIARY OF GULF RESOURCES & CHEMICAL CORPORATION

ORIGINATOR:
DISTRIBUTION:

	THIS	REPLACES
FILE:	1500-450	
DATE:	4/2/79	
PAGE:	11 OF 11	OF

MATERIAL SAFETY DATA SHEET

SECTION I

MANUFACTURER'S NAME Lithium Corporation of America	EMERGENCY TELEPHONE NO. 704-629-2282
ADDRESS (Number, Street, City, State, and ZIP Code) Hwy. 161 P.O. Box 795 Bessemer City, NC 28016	
CHEMICAL NAME AND SYNONYMS Lithium Metal - Technical Grade	TRADE NAME AND SYNONYMS Lithium Metal
CHEMICAL FAMILY Alkali Metal	FORMULA Li

SECTION II HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS		%	TLV (Units)	ALLOYS AND METALLIC COATINGS		%	TLV (Units)
PIGMENTS	N/A			BASE METAL	N/A		
CATALYST	"			ALLOYS	"		
VEHICLE	"			METALLIC COATINGS	"		
SOLVENTS	"			FILLER METAL PLUS COATING OR CORE FLUX	"		
ADDITIVES	"			OTHERS			
OTHERS							

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	TLV (Units)
N/A		

SECTION III PHYSICAL DATA

BOILING POINT (~~°F~~) (°C)	1317.0	SPECIFIC GRAVITY (H_2O=1) density g/ml	0.534
VAPOR PRESSURE (mm Hg.) (20°C)	nil	PERCENT VOLATILE BY VOLUME (%)	
VAPOR DENSITY (AIR=1) melting point (°C)	180.5	EVAPORATION RATE (________=1)	
SOLUBILITY IN WATER	reacts violently		
APPEARANCE AND ODOR light silvery metal; odorless			

SECTION IV FIRE AND EXPLOSION HAZARD DATA

		Lel	Uel
FLASH POINT (Method used) 871°C	FLAMMABLE LIMITS		

EXTINGUISHING MEDIA dry lithium chloride; graphite powder, Pyrene G-1

SPECIAL FIRE FIGHTING PROCEDURES Keep lithium metal fire confined as much as possible to a small area; cover with dry lithium chloride.
Water, moist sand, carbon dioxide or acid-soda ash fire extinguisher should not be used.

SECTION V HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE N/A - reactive alkali metal

EFFECTS OF OVEREXPOSURE Contact with skin or the eyes may result in caustic irritation and burn; molten lithium causes severe burns.

EMERGENCY AND FIRST AID PROCEDURES Skin - flush thoroughly with abundant water; consult a physician. In case of eye contact, flush with copious amounts of water for twenty (20) minutes; consult an ophthalmologist.

SECTION [illegible] REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	

INCOMPATABILITY (Materials to avoid) water and alcohols

HAZARDOUS DECOMPOSITION PRODUCTS Reacts with water to liberate hydrogen and form caustic lithium hydroxide.

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED With dry rubber gloves, pick up the lithium ingot and return to steel container and store under oil; label or tag. Keep away from moisture or water.

WASTE DISPOSAL METHOD Return to steel drum and store under oil until disposal time; label or tag. Dispose according to local or state EPA waste disposal regulations.

SECTION VIII SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type) normally not needed

VENTILATION	LOCAL EXHAUST	SPECIAL
	MECHANICAL (General)	OTHER

PROTECTIVE GLOVES plastic or rubber or asbestos

EYE PROTECTION safety goggles and face shield

OTHER PROTECTIVE EQUIPMENT rubber apron; fire retardant coveralls

SECTION IX SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING Store at room temperature in dry place; avoid exposure to water.

OTHER PRECAUTIONS Drums of oil coated lithium ingots should be rotated end for end twice a month.

Prepared by ______________________

PRODUCT BULLETIN

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LITHIUM METAL

HANDLING, STORAGE, AND SAFETY PRECAUTIONS

Due to the chemical activity of lithium, special methods must be used in handling and storing the metal.

1. Safety Precautions

All personnel handling lithium should be thoroughly instructed as to the hazards involved. Most accidents resulting from the use of lithium occur among inadequately trained employees.

Care should be taken to prevent bodily contact with lithium metal. Solid lithium may be handled by using rubber or plastic gloves or with metal tongs. Contact with the skin or eyes may result in a caustic irritation or burn. Thorough flushing with water and treatment with boric acid is a satisfactory first aid procedure. For handling molten lithium workmen should be protected with flame-proof clothing, foundry-type shoes, asbestos gloves, and a head shield. One type of head protection consists of an aluminum shield covering the front, sides and top of the head. A clear plastic window is set in the front. A flame-proof bib of canvas extending down from the front of the shield to cover the chest area protects the wearer from metal spattering on the chin and neck. It must be emphasized here that there is no known fabric which will offer complete protection against burning lithium. However, if clothing is flame-proofed the area of burn will be minimized. In case of a burn from burning metal, the area should be flooded with a liberal amount of mineral oil. The metal should be removed as quickly as possible by scraping with a sharp edged object. The injured person should be treated at once for shock and referred to competent medical aid.

Liquid lithium is quite easily ignited and once burning is difficult to extinguish. Hot or burning lithium will react with all gases except those of the helium-argon group. It also reacts violently with concrete, wood, asphalt, sand, asbestos, in fact, with nearly everything except metal.

Burning lithium may be extinguished by smothering with dry powdered lithium chloride, graphite powder, or Pyrene G–1. Water, sand, carbon tetrachloride, carbon dioxide, or acid-soda extinguishers should not be used. The inert gases are not very effective unless the fire is confined to a container which can be sealed off. A supply of one or more of the approved materials, together with a long handled shovel for application to the fire, should be available wherever lithium is stored or used.

A comprehensive discussion of safety practices for handling lithium is contained in the following publication: "Alkali Metals Area Safety Guide", by Preston L. Hill, published by the Y–12 Alkali and Liquid Metals Safety Committee of the Atomic Energy Commission, Oak Ridge, Tennessee.

2. Solid Lithium Metal

Lithium metal is normally supplied as a casting or extrusion of size and shape best suited to the user's needs. These shapes include ribbon, wire and ingots of various weights and dimensions.

Solid lithium is less active than the molten metal. However, its activity increases sharply as its temperature approaches the melting point. Therefore, handling methods, hazards and precautions depend to some extent upon the temperature at which it is used.

a. Room Temperature

Lithium metal is usually stored at room temperature. Precautions must be taken to avoid exposure to water and other materials with which it may react and to prolonged exposure to air. The metal is generally stored in metal drums, and surrounded with an inert material. The material most commonly used is a refined white mineral oil, although kerosene and other light petroleum fractions are used. A suitable white mineral oil with a high flash point is 105 BT 40 white oil, L. Sonneborn Sons, Inc., 9 South Clinton, Chicago, Illinois. Where hydrocarbons cannot be tolerated, the metal may be stored in drums filled with dry inert gases such as argon, helium or certain fluorocarbons. Lithium wire and ribbon are often protected by a heavy coating of petrolatum.

When mineral oil is used as the protective medium for storage of lithium metal, the ingots may either be totally submerged in an excess of oil, or they may be merely coated with a protective film. Total submergence in airtight containers is a positive means of storing the metal for long periods. For practical reasons it is often desirable to store the metal with only the protective film. This is done by packing the ingots in a steel drum, pouring in enough oil to coat the metal and provide a 2--3 inch layer of oil at the bottom, and by rotating the drum at least twice a month. Metal so packed may be satisfactorily stored for several months. Most drums are not air-tight so that in spite of the oil film a slow deterioration of metal will occur. For this reason, lithium metal which is to be stored for periods longer than 2—3 months should be kept totally submerged in mineral oil in air-tight containers or, as an alternate, in air-tight drums filled with a suitable inert gas. Thus protected lithium metal will remain in good condition indefinitely.

In most cases, before the metal is used it is necessary to remove the protective coating of oil or petroleum. Hydrocarbon solvents, such as Stoddard's solution, may be used with normal precautions. Ethers, alcohols, unsaturated hydrocarbons or any solvent containing moisture must not be used. While carbon tetrachloride has been used, particularly for preparing laboratory samples, its use is not recommended because explosive reactions have occurred when used similarly for cleaning sodium metal. Degreasing is carried out by gently agitating the metal in the solvent, draining off the excess, and drying in air.

Freshly cut, cast, or extruded lithium exhibits a bright silvery surface, which on exposure to ordinary air quickly darkens and becomes quite black, although for some time this will be only very superficial. (This black coating is probably not nitride, as commonly supposed, but hydroxide. See Deal and Svec, J. Am. Chem. Soc. 75, 6173, 1953.)

On prolonged exposure reactions proceed with the oxygen, moisture, and carbon dioxide of the air to form LiOH and Li_2CO_3. Even when coated with an oil film, the reaction with air will proceed slowly with the ultimate formation of a slimy coating of oil and lithium hydroxide. All of these alteration products which may have formed during storage should be removed by scraping before use to prevent contamination and hazard, particularly when the metal is to be melted.

It has been noted that when lithium metal is stored dry in a container which is not entirely air-tight, the deterioration product is a dense, brittle, reddish brown material, probably largely lithium nitride. This is in marked contrast to the soft, white hydroxide and carbonate product which forms when the dry metal is left freely exposed to the atmosphere at room temperature.

Metal drums, reaction vessels, tools, and any ferrous metals with which lithium metal is liable to come in contact should be free of rust. When lithium is rubbed against a rusty surface, sparks often result, creating an explosion hazard if inflammable gases are present.

Lithium metal may be readily cut in air at room temperature without danger of fire. A coating of oil on the cutting blade will help to prevent the metal from adhering to the tool.

b. Elevated Temperature

Notable differences between the activity of lithium at room temperature and at temperatures approaching the melting point are its affinity for nitrogen and its reaction with water.

At ordinary room temperature lithium reacts very slowly with nitrogen, but at higher temperatures this reaction is greatly accelerated. Warm lithium metal, when not adequately protected with oil or an inert gas, may be completely converted in a relatively short time to a heavy reddish-brown solid consisting largely of lithium nitride. Although the reaction is exothermic, it does not usually proceed rapidly enough to melt the metal or cause it to ignite.

Special care must be taken to avoid contact of water with hot lithium. Cold lithium reacts slowly with water and the hydrogen formed seldom, if ever, ignites. The reaction is much more vigorous and dangerous at elevated temperatures, and enough heat may be generated to ignite the hydrogen causing fire and possible explosion.

3. Liquid Lithium Metal

Molten lithium metal is much more active than the solid, but it may be readily and safely handled if the proper precautions are observed.

At low temperatures (190—225°C.) lithium may be melted in an electrically heated mineral oil bath with automatic temperature control. The molten metal will float on the oil but, due to surface tension effects, it will have a protective film of oil. At times during the melting operation it is desirable to renew the oil film by gentle stirring with a steel rod or by dripping a little oil directly onto the metal surface. Transfer of the metal from the melting pot may be made with a steel or stainless steel ladle or by means of a pouring spout on the pot.

If it is desired to melt lithium at temperatures above 225°C., an oil bath cannot be used. This is best done in a closed steel vessel in which an inert atmosphere of argon or helium can be maintained.

4. Lithium Scrap

In handling and using large quantities of lithium metal some scrap will accumulate such as small pieces of left over metal, scrapings, process by products containing unreacted lithium, sludge from melting operations, nitrided metal, and partially burned metal. Disposal of such material often presents problems. Small pieces of metal can of course be sorted out, stored and reused. When metal is melted a sludge separates out which is composed of nitrides, oxides, and possibly carbides under certain conditions, together with some trapped metal. Scrap from partially burned metal may contain oxides, nitrides, carbides, silicates, salts, etc., depending upon the nature of the material which has come in contact with the burning metal.

All such sludges and residues should be stored under oil until they can be disposed of. In general, it is difficult if not impossible to recover the small amount of lithium metal present. In most cases the only practical method of lithium recovery is by water leaching with the resultant conversion of the metal, carbides, nitrides, etc., to lithium hydroxide. At best this is still a hazardous operation. The hydrogen formed, together with small amounts of acetylene from the carbides present, may ignite with a resulting sharp explosion. Therefore, this operation should be carried out in an open vessel, isolated from building and personnel. The remaining alternative is to burn the material in a suitable disposal area.

Residual lithium adhering to containers, reaction vessels and tools can usually be washed with water provided that the quantity of metal is not excessive, the equipment to be cleaned is at room temperature, and there are no lithium sludge products present whose activity with water is excessive or unknown. Generally, water cleaning is best done out of doors.

5. Materials of Construction

Comprehensive data is not available as to the effects of lithium on various materials. Tests have been made on a great many different materials of construction but in many cases the results are qualitative only. Where corrosion occurs it is not always known whether the effect is due to lithium itself or to its normal content of impurities. For most ordinary uses where lithium is to be stored or melted, mild steel is satisfactory. A number of metals are listed below with a qualitative description of their resistance to lithium. Part of this data is taken from the "Liquid Metals Handbook", Lyon, Richard N., Atomic Energy Commission, Department of the Navy, Washington, D. C., 2nd edition, 1952.

a. Armco Iron – Good up to 600°C. and in some cases up to 1000° C. and higher.

b. Stainless Steel – Good up to 500°C. At temperatures above 500° C. the resistance varies according to conditions. Ladles of stainless steel 302 and 304 used for dipping molten metal at temperatures of about 550° C. have shown no corrosion after more than a year of use.

c. Low Carbon Steels – Good resistance up to 700° C. depending on conditions. In melting pots where the temperature has not exceeded 240°C. some attack is evident after prolonged use. The attack appears greatest at the point where accumulated sludge has been in contact with the walls of the pot. Attack by molten lithium nitride is known to be severe.

d. Refractory Metals – Columbium, tantalum, and molybdenum show good resistance at 1000° C., zirconium and titanium fair resistance, while vanadium, beryllium, and chromium are severely attacked.

e. Nickel and Nickel Alloys – Nickel has good resistance to attack at 225° C., limited resistance at 300°C. and poor resistance at 600°C. or higher. Chromel wire showed poor resistance at 700°C. Monel A, Hastelloy B and Nichrome V were corroded at 315° C.

f. Other Metals – Aluminum, barium, bismuth, calcium, cadmium, gold, lead, magnesium, platinum, silicon, silver, strontium, thallium, tin and zinc react with molten lithium to form products of no structural usefulness. Copper and copper alloys such as aluminum bronze have poor resistance. Manganese, silicon, and high-temperature cobalt base alloys are also attacked by molten lithium.

g. Non-metals – Quartz is attacked at temperatures above the melting point of lithium, as is glass, porcelain, and other silicate materials. Molten lithium penetrates magnesia but does not attack it. Molten lithium attacks oxides of most structural metals, as well as carbides, silicides, rubber, and plastics.

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The information contained in this bulletin is believed to be accurate and reliable. However, it is presented without guarantee or responsibility on the part of Lithium Corporation of America. Furthermore, nothing contained herein shall be taken as a recommendation to manufacture or use any material in violation of existing or future patents.

R 4.5.6 "Flammable Solid" and "Dangerous When Wet" labels on the outside container.

5.0 SAFETY- OSHA

5.1 Hazard Analysis

Elemental lithium, a soft silvery metal, is the lightest of the normally solid elements. It is the least active of the alkali metals and reacts slowly with cold water. Near the melting point lithium may ignite in air, burning with an intense white flame.

The reactivity of lithium metal is the chief hazard encountered in storing and handling. Care should be taken to prevent bodily contact with lithium metal. Solid lithium can be handled by using rubber or plastic gloves or with metal tongs. Contact with the skin or eyes may result in a caustic irritation or burn.

Liquid lithium is quite easily ignited and once burning is difficult to extinguish. Hot or burning lithium will react with all gases except those of the helium-argon group. It also reacts violently with concrete, wood, asphalt, sand, asbestos, in fact, with nearly everything except metals such as iron or steel.

Burning lithium can be extinguished by smothering with dry powdered lithium chloride, graphite powder, or Pyrene G-1. Water, sand, carbon tetrachloride, carbon dioxide, or acid-soda extinguishers should not be used. The inert gases are not very effective unless the fire is confined to a container which can be sealed off. A supply of one or more of the approved materials, together with a long handled shovel for application to the fire, should be available wherever lithium is stored or used.

5.2 Safety Precautions

Where lithium is being handled and there is danger of spillage, full protective clothing is prescribed. Goggles which provide adequate protection against flying solids and liquids should be worn when lithium or equipment containing lithium is being handled. Proper gloves, flame-proofed garments and head covering give maximum protection. Where lithium in solid form such as bricks is used and there is no danger of spillage, proper protective clothing to suit the conditions should be worn. Face shields protect the entire face in cases where other hazardous products are possibly present.

If lithium is sprayed on any considerable area of the clothing, garments should be removed immediately.

5.3 Treatment

Lithium burns on the skin are of the same nature as caustic burns and require immediate first aid treatment. They must be washed with large volumes of clear tap water for at least 15 minutes. If any particles of lithium adhere to the skin, they should be quickly brushed off before washing to avoid additional burning from the heat of reaction of lithium and water. After washing, the affected skin area should be coated with a sterile bland ointment dressing and medical attention sought. Further treatment of the burn should be prescribed by the examining physician.

Eye burns should be treated immediately by flushing the eyes with copious amounts of tap water for at least 15 minutes and medical treatment should be given promptly.