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A Micrographic Comparison of Greases:

STRATCO® Contactor™ Reactor vs. Kettles

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Introduction

It has been very well established and reported in previous technical papers that the use of a Contactor reactor can improve the yield of greases [1][2]. Although logic dictates that this improvement results from structural differences in the fibrous matrix of the thickeners, such a difference has yet to be explored photographically to any great extent. Although there have been numerous books, articles and technical papers written, which illustrate grease structures via electron micrographs, the authors of this paper are aware of only one comparison study of grease structures resulting from different manufacturing methods [3], which was limited to simple lithium grease with the samples not clearly identified as being produced on a laboratory or commercial scale. Also, the micrographs presented in that study were very limited in number and clarity. Therefore, the purpose of this paper is to present micrographic comparisons of several common grease types, which are manufactured commercially using three different types of reactors: (1) the STRATCO® Contactor™ reactor, (2) the autoclave and (3) the open kettle.

The strategy of this study is to provide micrographic comparisons of greases which were manufactured on a commercial scale, so as to be truly representative of greases sold in the market place. Although it was desired that the greases from the various sources be similar in regards to the raw ingredients used, this proved to be impractical owing to the variety in formulations from one manufacturer to another. The study still proves to be valid if consideration is given to the variety of raw materials. Consequently, control batches on a lab scale are produced which do utilize identical raw ingredients so that a true “apples to apples” comparison can be illustrated. As would be expected, structural differences can also result from variances in temperature profiles as well as the reactor type and related means of agitation. However, it should be recognized that the samples included in this study are representative of typical commercial greases produced by the types of reactors mentioned and the comparisons will prove useful in evaluating the effectiveness of the reactors.

Although the Contactor reactor has been used to manufacture most types of greases, this study is limited to only the most common types of greases, namely lithium, lithium complex, calcium and aluminum complex. The samples of lithium, lithium complex and calcium were obtained from all three methods, while aluminum complex samples are limited to the Contactor reactor and autoclave. Laboratory samples were produced of only the lithium grease using the Contactor reactor and an open kettle. Dropping points, 60-stroke penetration and 10,000-stroke penetrations were measured by STRATCO, Inc. and are presented for reference. There were a few instances where values provided by the producer differed slightly from STRATCO’s measurements and these are indicated in the data.

Grease Sample Preparation and Micrography

Grease samples were obtained from three different manufacturers in order to obtain samples from the different reactor types. In most cases, the samples were obtained in their basic form, without dyes or additives. They were tested for dropping point using ASTM D 2265 and penetration using D 217. Small amounts of these samples were sent to a laboratory for micrographic analysis. The basic preparation included placing a thin film on an aluminum pan, which was immersed in hexane for approximately 30 minutes. The residual thickener was then gold sputtered for approximately two minutes to make the samples electrically conductive. A field emission Scanning Electron Microscope was used to photograph the samples in order to get high resolution images.

Simple Lithium Grease

It is worthwhile to note the differences in the raw ingredients used for these three sample greases studied. The greases produced in the autoclave and open kettle utilized only 12 hydroxystearic acid (12HSA) while the grease produced in the Contactor reactor predominantly used hydrogenated castor oil (HCO) in combination with 12HSA. Table 1 provides some additional properties of these samples.

Reactor Type	Dropping Point °F (°C)	Penetration (60 stroke)	Penetration (10K stroke)	Soap Content (%)
Contactor reactor	394 (201.1)	292	293	7.7 – 8.0 (9.0)
Autoclave	401 (205)	266	279	7 – 8
Open Kettle	402 (205.5)	277	287	7.6

Table 1: Sample Lithium Grease Properties

Previous lab studies [4] have shown that greases manufactured with HCO could require from 23% to 44% higher soap content compared to 12HSA based lithium grease in order to attain comparable properties. Therefore, the properties shown are understandable and expected. However, it is worthwhile to note that the soap content presented by the manufacturer for the Contactor reactor (shown in parentheses) is based upon the total mass of the reactants. If the basis were adjusted to eliminate the mass of the glycerol and water produced in the reaction, the actual soap content would be reduced to between 7.7% and 8%. Very notable is the insignificant change in penetration between the 60 stroke and 10,000 stroke conditions, which suggest a very shear stable structure.

Figure 1 provides micrographic comparisons at a magnification of 50,000X and Figure 2 provides similar comparisons at a magnification of 20,000X. The images of greater magnification are of a boundary region to provide greater detail of individual fibers. The lesser magnification images are presented to convey a better representation of the general fiber matrix. This latter comparison indicates that the fiber matrix in each case is formed of long fibers with a large length to diameter ratio. Such fibers will tend to form a more effective matrix considering that the long fiber lengths and relatively thin diameters allow more points of contact and greater opportunities to entangle, producing a strong mesh for retaining the lubricating oil. It also seems apparent that, for all three samples, the fibers provide a variety of fiber thicknesses. C. J. Boner states [5] that large length to diameter ratios contribute to shear stability while very small fibers are more effective in holding the lubricating oil. Consequently, a structure with both of these characteristic fibers is the most desirable. However, a close study of the micrographs indicates that the Contactor reactor grease appears to be composed of generally thicker fibers.

Figure 1: Lithium Grease at 50,000 X magnification

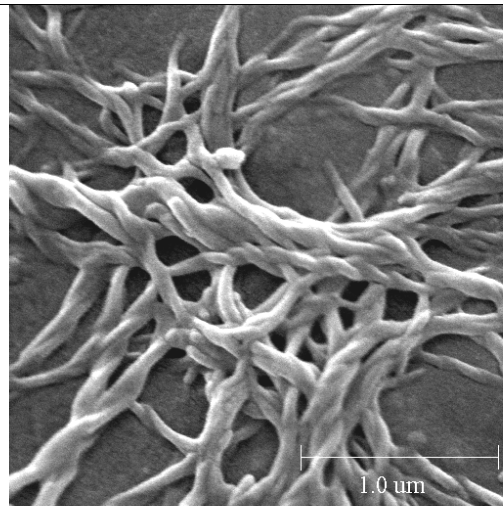
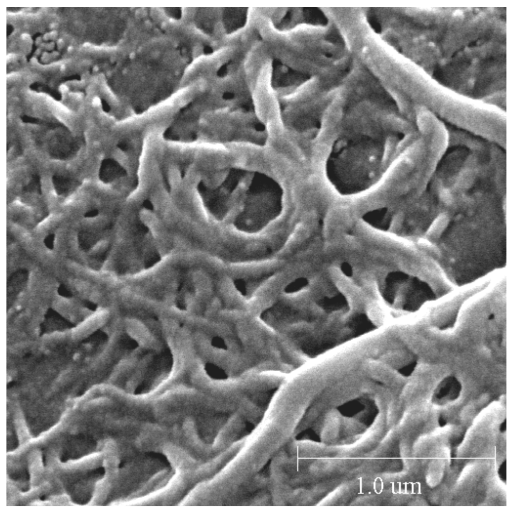
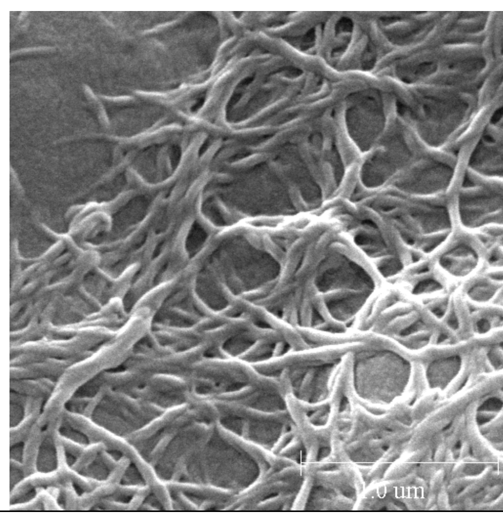
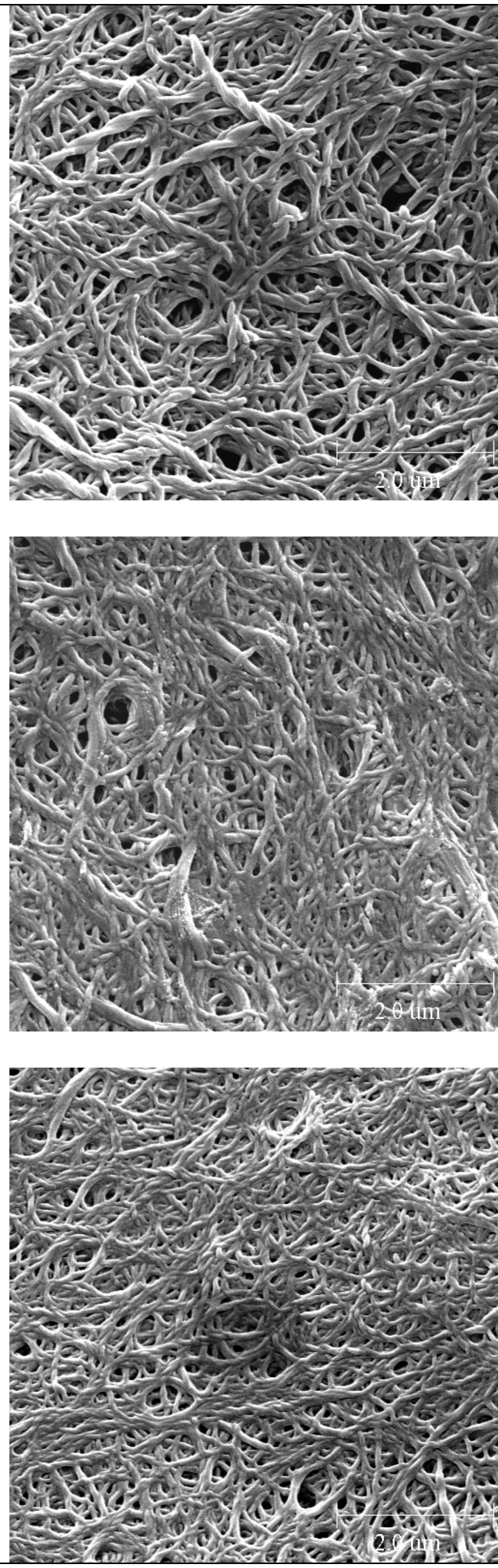
STRATCO® Contactor™ Reactor	
Open Kettle Process	
Autoclave Process	

Figure 2: Lithium Greases at 20,000 X magnification

STRATCO® Contactor™ Reactor

Open Kettle Process

Autoclave Process



Laboratory Simple Lithium Greases

The lithium greases produced in the lab were limited to the Contactor reactor and open kettle method and were produced from 12HSA. Table 2 presents properties of these greases. The same 12HSA, lithium hydroxide and base oils were used in both methods. Unexpectedly, the yield for the open kettle process is slightly greater for identical soap contents. Although historically the Contactor reactor grease would result in the greater yield, this particular instance resulted in the contrary. However, it is worthwhile to note the differences in manufacturing these two batches. The Contactor reactor batch was completely processed in 4 to 5 hours, with the cooling rate regulated at 0.6°F/minute between 360°F and 325°F. The open kettle batch was saponified and cooled to 200°F in about 8 hours, also with the cooling rate regulated at 0.6°F/minute between 360°F and 325°F. The following day, the batch was reheated to 190°F to achieve circulation for milling, which all took an additional 2 to 2.5 hours. It is assumed that the additional processing of the open kettle sample contributed to the unexpected results in yield. (The lower 60-stroke penetration was measured at the manufacturer's laboratory.)

Reactor Type	**Dropping Point °F (°C)**	**Penetration (60 stroke)**	**Penetration (10K stroke)**	**Soap Content (%)**
Contactor reactor	394 (201.1)	255	270	8.0
Open Kettle	398 (203.3)	235 - 240	245	8.0

Table 2: Lab Scale Simple Lithium Grease Properties

Figure 3 presents micrographs of the grease produced in the Contactor reactor and Figure 4 shows the grease produced in the open kettle. Similar to the commercial scale samples, both methods produce a well developed structure of long and relatively thin fibers with a good variety of fiber diameters. An interesting observation is illustrated in Figure 3 concerning the nature of these grease fibers. The thinner fibers that cross over the relatively large diameter fiber oriented vertically in the image appear almost fused to the surface for about 180°. This clearly indicates the very limp nature of the fibers and may indicate a significant adhesive quality of the fiber's surface.

Figure 3: Lithium Grease made in the STRATCO® Contactor™ Reactor (Lab Scale)

20,000 X **50,000 X**

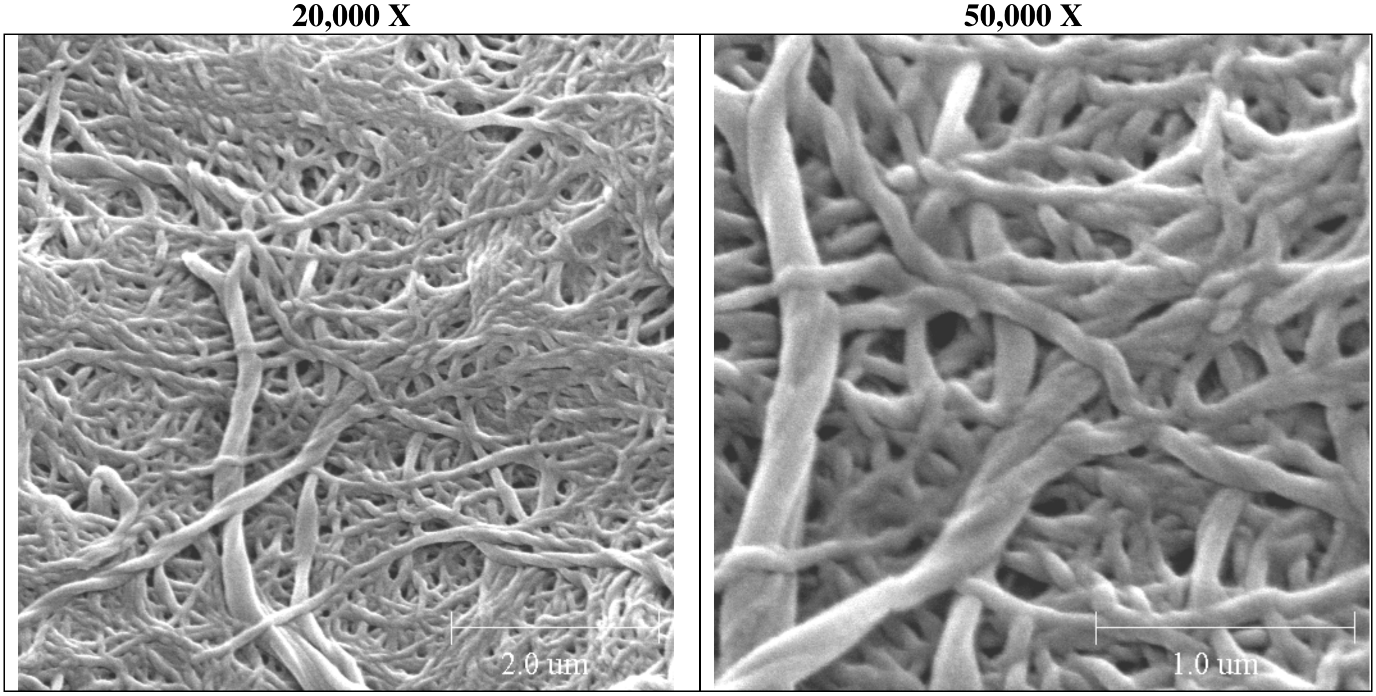
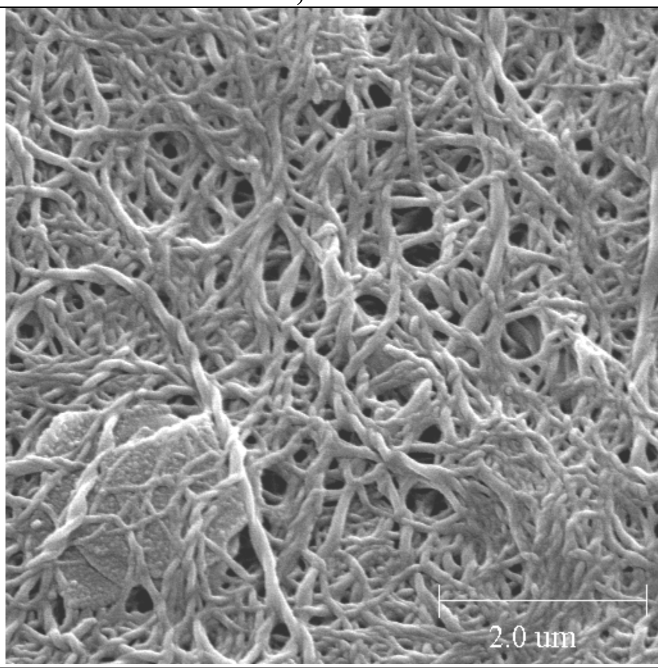
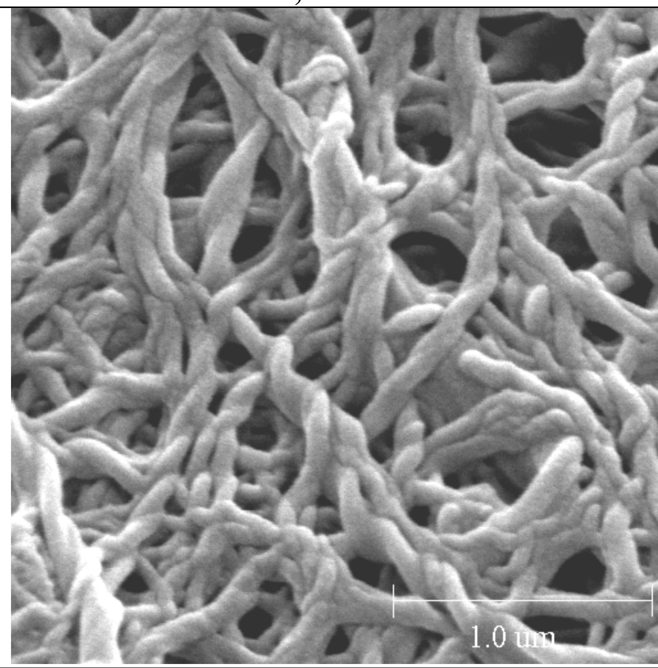


Figure 4: Lithium Grease made in an Open Kettle (Lab Scale)

20,000 X	50,000 X
	

<u>Lithium Complex Grease</u>

All of the lithium complex greases tested are produced from the use of 12HSA. It is also worth noting that the Contactor reactor grease utilized sabacic acid as the complexing agent, while the other two samples utilized azelaic acid, which may have some affect on the structure. Table 3 presents properties for these greases. Previous studies have shown that using the Contactor reactor allows the reduction of soap content as compared to a conventional kettle operation. As with the previous commercial Contactor reactor sample, the soap content shown in parentheses is based upon total mass of the reactants and the lower soap content removes the mass of the water evolved. (The lower 60-stroke penetration for the open kettle sample was measured at the manufacturer's laboratory.)

Reactor Type	Dropping Point °F (°C)	Penetration (60 stroke)	Penetration (10K stroke)	Soap Content (%)
Contactor reactor	545 (285)	282	286	13.47 (16.0)
Autoclave	532 (277.8)	278	281	18 - 19
Open Kettle	526 (274.4)	271 - 282	293	13.87

Table 3: Sample Lithium Complex Grease Properties

Figures 5 and 6 present micrographic comparisons at 50,000X and 20,000X, respectively. As previously, we have shown the greater magnification images near the sample boundary to offer greater detail of individual fibers. All samples again appear to form well woven networks of long fibers. Figure 5, which displays images from the core area of the samples, shows a distinct difference between the autoclave grease and the other two. This distinction appeared consistent throughout the samples. Although it is not apparent whether this distinction is chemical, physical or both, there does seem to be a difference. The micrographs reveal that the fibers of the autoclave grease tend to be straight, while the fibers of the other two greases include significant quantities of fibers with twists. Also, extremely thin fibers are much more prevalent in the autoclave sample and the Contactor reactor sample appears to be composed of thicker fibers than the other two.

Figure 5: Lithium Complex Greases at 50,000 X magnification

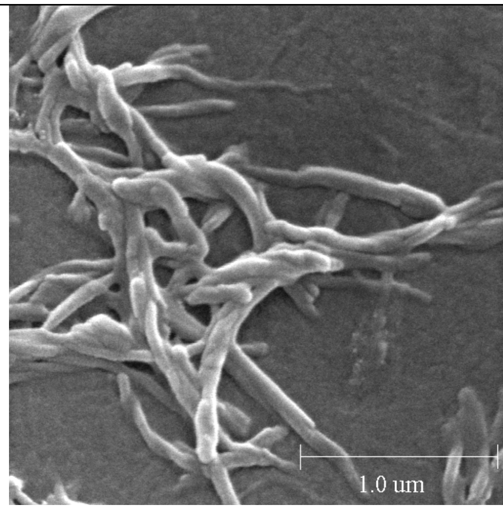
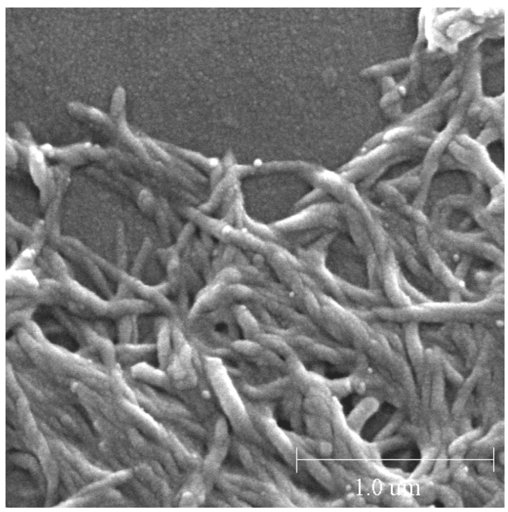
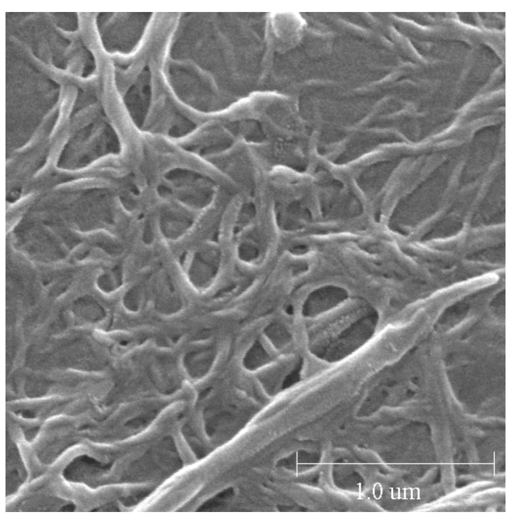
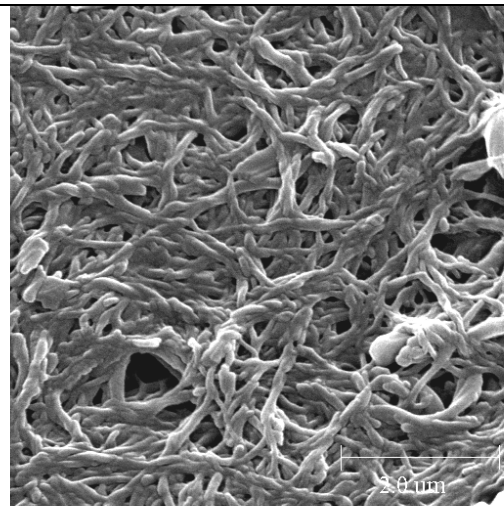
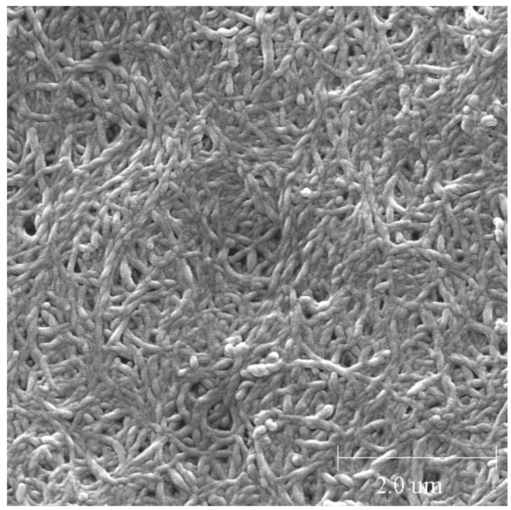
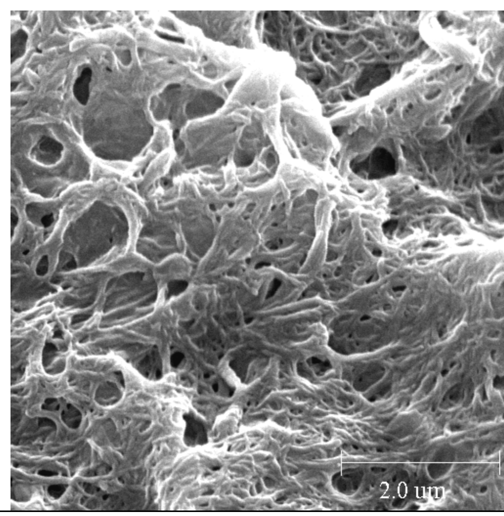
STRATCO® Contactor™ Reactor	
Open Kettle Process	
Autoclave Process	

Figure 6: Lithium Complex Greases at 20,000 X magnification

STRATCO® Contactor™ Reactor	
Open Kettle Process	
Autoclave Process	

Calcium Grease

The calcium greases obtained were produced with all three reactor methods. Although our goal was to obtain samples manufactured from the same raw ingredients, we were unable to meet this goal. In fact, the Contactor reactor and open kettle samples were manufactured using 12HSA, which is an anhydrous calcium grease, and the autoclave grease was manufactured from tallow, which is a hydrated calcium. Table 4 presents the properties for these grease samples. The properties associated with these samples are as expected according to the types of greases produced, e. g. the relative dropping points and relative soap contents. (Please note that the unexpectedly low 60-stroke penetration of the Contactor reactor sample is probably in error and, unfortunately, could not be reproduced since the entire sample amount was subsequently subjected to 10,000 strokes.) Also, it is important to note that the soap content shown for the Contactor reactor, which was provided by the manufacturer, includes the mass of the water evolved in the process, whereas the soap content associated with the open kettle does not. Adjusting the soap content of the Contactor reactor grease to the same basis as the open kettle grease reduces the actual soap content to approximately 8.7%, or 2% less than the open kettle soap content.

Reactor Type	Dropping Point °F (°C)	Penetration (60 stroke)	Penetration (10K stroke)	Soap Content (%)
Contactor reactor	304 (151.1)	234 (!)	262	8.7 (9.15)
Autoclave	220 (104.4)	284	291	16 - 18
Open Kettle	304 (151.1)	262	274	10.7

Table 4: Calcium Grease Properties

Figure 7 presents micrographs of the anhydrous calcium grease produced in the Contactor reactor and Figure 8 shows the hydrated calcium grease produced in the autoclave. These micrographs tend to be more representative of a comparison of two different grease types than a comparison of greases from different reactor types. (Actually, we had expected the autoclave sample to be an anhydrous calcium grease and the fact that it was a hydrated calcium was discovered only after we obtained the micrographs and the subsequent dropping point measurements and questioned its chemistry.) Fortunately for our study, we were able to obtain an open kettle sample of an anhydrous calcium grease. This open kettle sample did incorporate the manufacturer's standard additives, but we were hopeful that the grease's fiber structure and appearance would still offer a beneficial comparison. This sample is shown micrographically in Figure 9.

With these micrographs we can establish that the fiber matrix of the anhydrous greases are well developed and include a good variety of long thin fibers. The structure of the hydrated calcium is comprised of relatively short fibers of a spiral form, which is typical of a hydrated calcium grease. Comparing the two anhydrous grease samples, it again appears that the Contactor reactor grease is composed of thicker fibers than the open kettle sample.

Figure 7: Anhydrous Calcium Grease made in the STRATCO® Contactor™ Reactor

20,000 X **50,000 X**

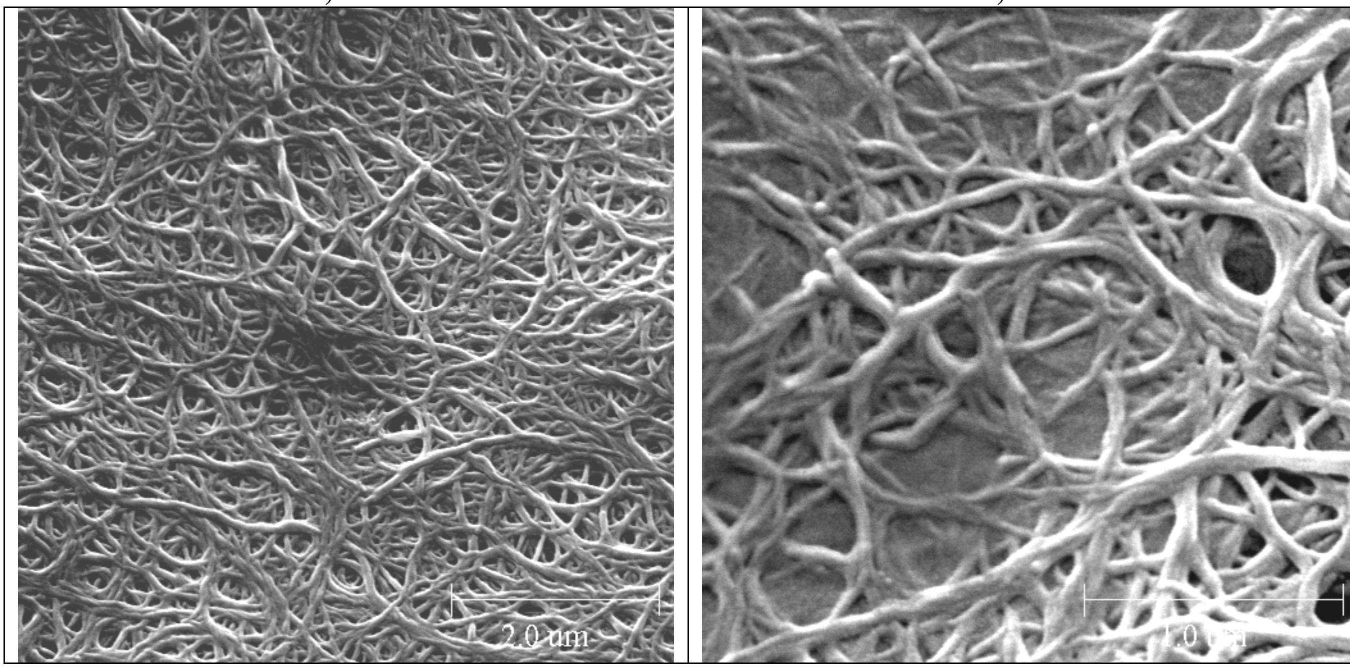


Figure 8: Hydrated Calcium Grease made in an Autoclave

20,000 X **50,000 X**

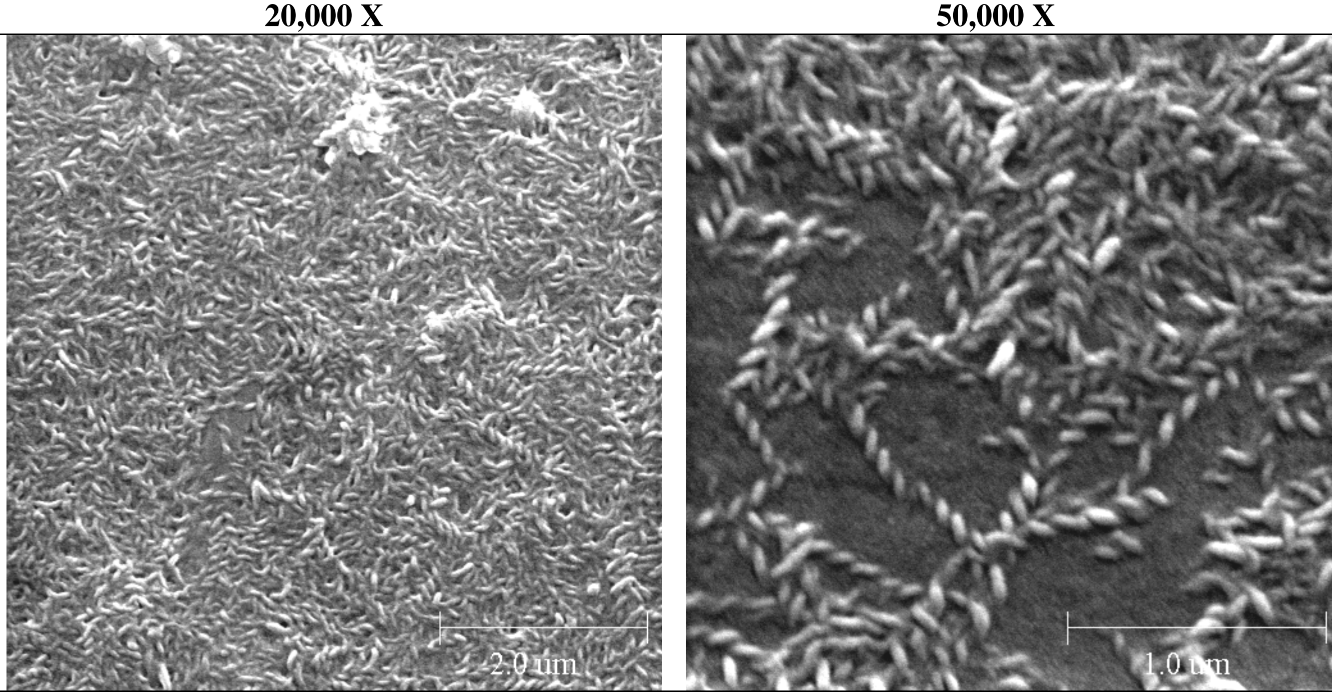
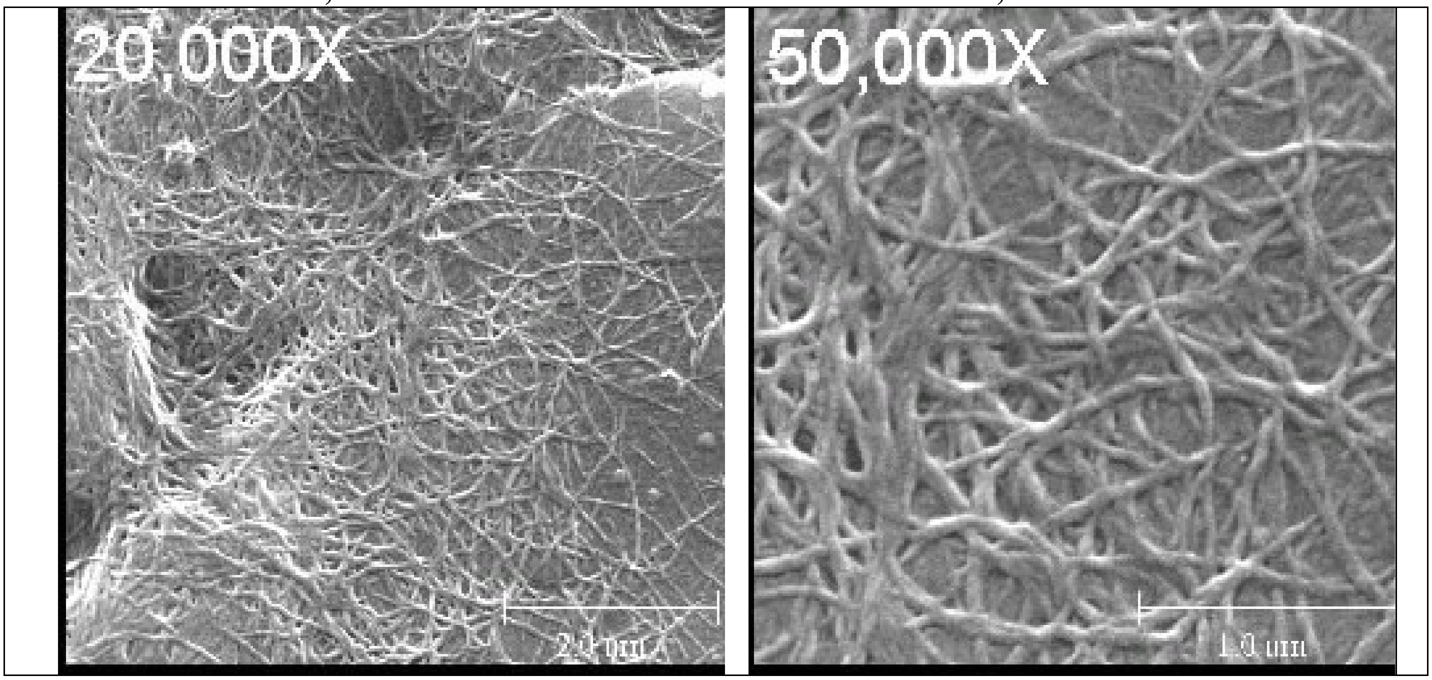


Figure 9: Anhydrous Calcium Grease made in an Open Kettle

20,000 X **50,000 X**



Aluminum Complex Grease

Aluminum complex grease samples were obtained from operations employing the Contactor reactor and an autoclave. Samples included both the food grade and non-food grade formulations. Table 6 presents the properties of these grease samples. As with the other Contactor reactor samples, the soap content provided by the manufacturer is based upon the total mass of the reactants. Using the reaction stochiometry to eliminate the evolved alcohol, the actual soap content is reduced to approximately 9%, which is significantly less than that of the comparable autoclave sample.

Reactor Type	Dropping Point °F (°C)	Penetration (60 stroke)	Penetration (10K stroke)	Soap Content (%)
Autoclave (food grade)	510 (265.5)	272	286	11 - 12
Contactor reactor (non-food grade)	495 (257.2)	264	298	9.08 (10.3)
Autoclave (non-food grade)	500(260)	219	265	11 - 12

Table 6: Aluminum Complex Grease Properties

Figure 12 presents micrographs of a Contactor reactor sample of non-food grade aluminum complex and Figure 13 presents micrographs of an autoclave sample of the same type of aluminum complex. The structure of the aluminum complex does not appear as a well developed string-like fiber, but resembles tufts of cotton-like fibers. There is no clear distinction between the two reactor types. Other methods of sample preparation were used in order to obtain a more defined image. In addition to the sample preparation procedure previously described, three other methods were used: (1) soaking the samples in Hexane for 5 hours, (2) soaking in Toluene for 30 minutes and (3) soaking in Hexane for 30 minutes followed by immersion in liquid nitrogen for one minute. All samples were gold sputtered as previously described. The fiber structures were still no more evident than with the original standard preparation. Indeed, in all of the existing literature observed by the authors, the appearance of the structure of this type of grease is very similar to our results.

Figure 12: Aluminum Complex Grease made in the STRATCO® Contactor™ Reactor

20,000 X **50,000 X**

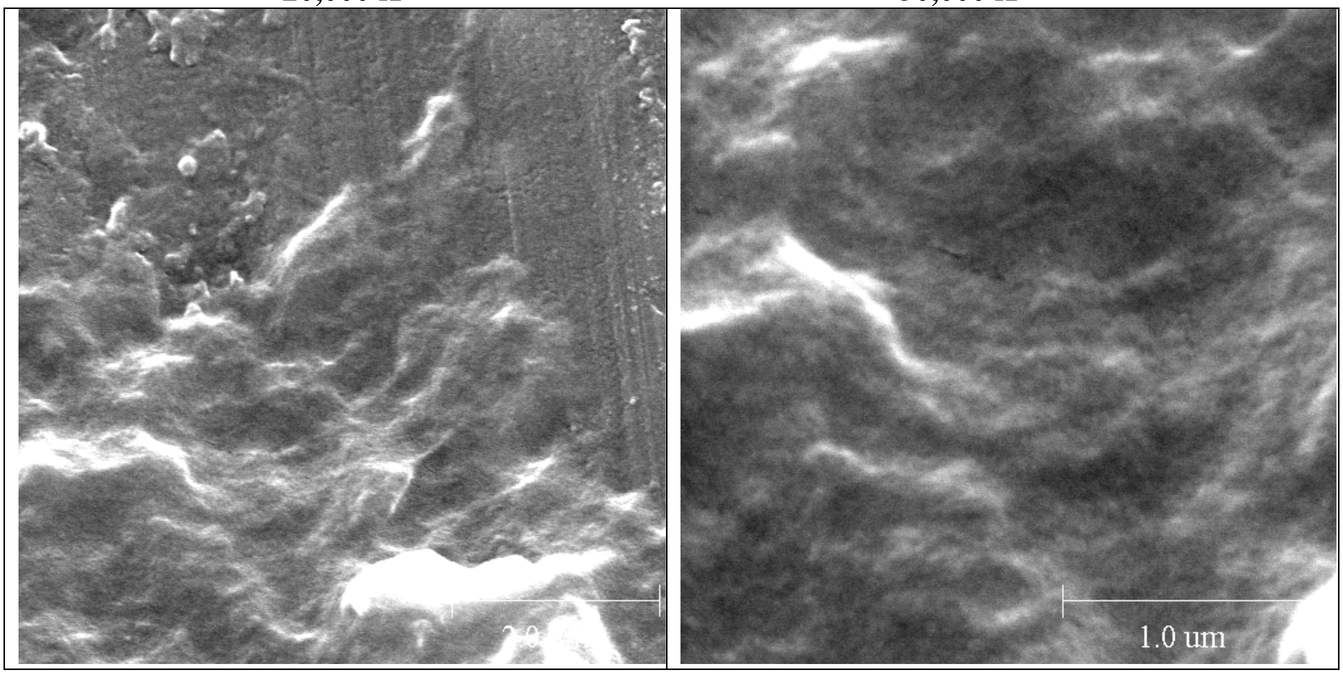
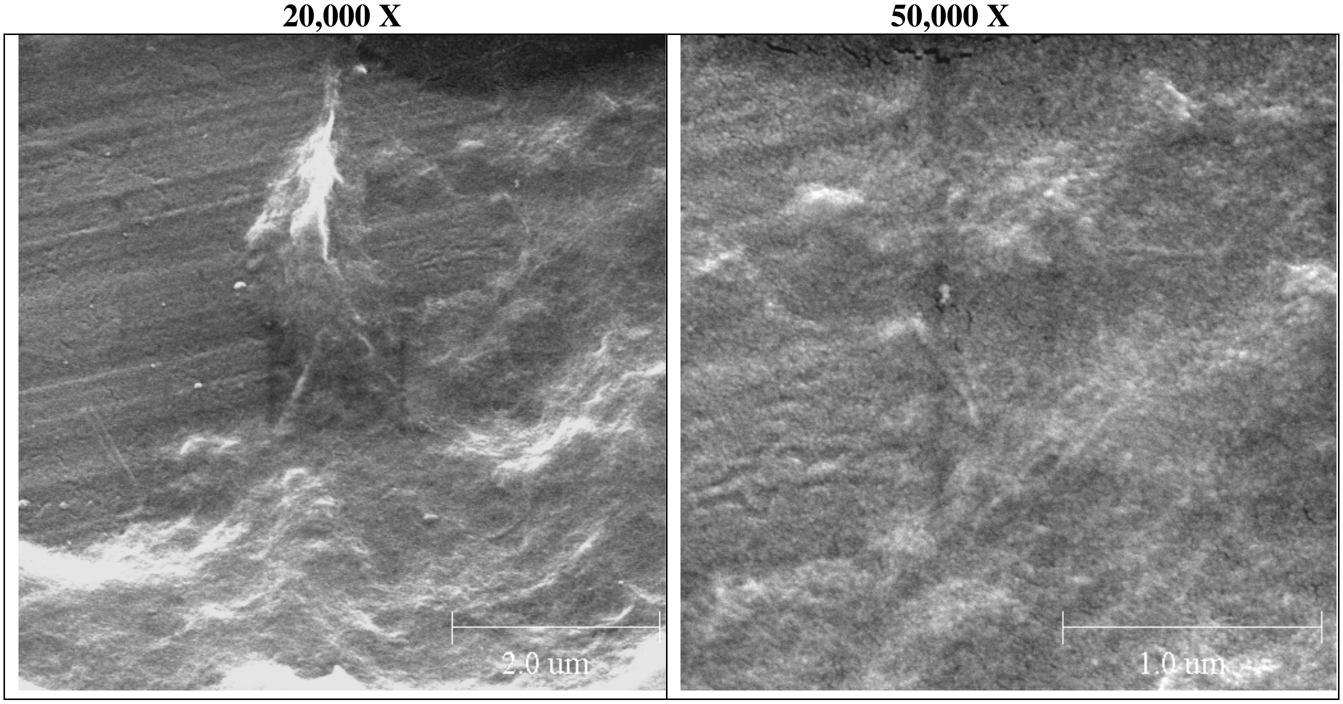


Figure 13: Aluminum Complex Grease made in an Autoclave

20,000 X **50,000 X**



Next, a technique known as critical point extraction was used. In this technique, grease samples placed on copper grids were contacted with liquid CO_2 at approximately 850 psig and 70°F. The temperature was then increased beyond the critical point. Soak time in liquid CO_2 was approximately 30 to 60 minutes. The resulting micrographs revealed some interesting structures. Figure 14 is from the autoclave and Figure 15 is from a Contactor reactor. These micrographs reveal a definite structure, which was nonexistent in the micrographs of the same magnification prepared in Hexane. It leads the observer to wonder if the Hexane technique might have destroyed the thickener chemically. If this is the case, these micrographs may be the only true representation of aluminum complex soap in published literature. The structure appears to be fused dough-like material. The sample from the autoclave seems to have a smoother surface texture than that of the Contactor reactor.

Figure 14: Aluminum Complex Grease made in an Autoclave

20,000 X **50,000 X**

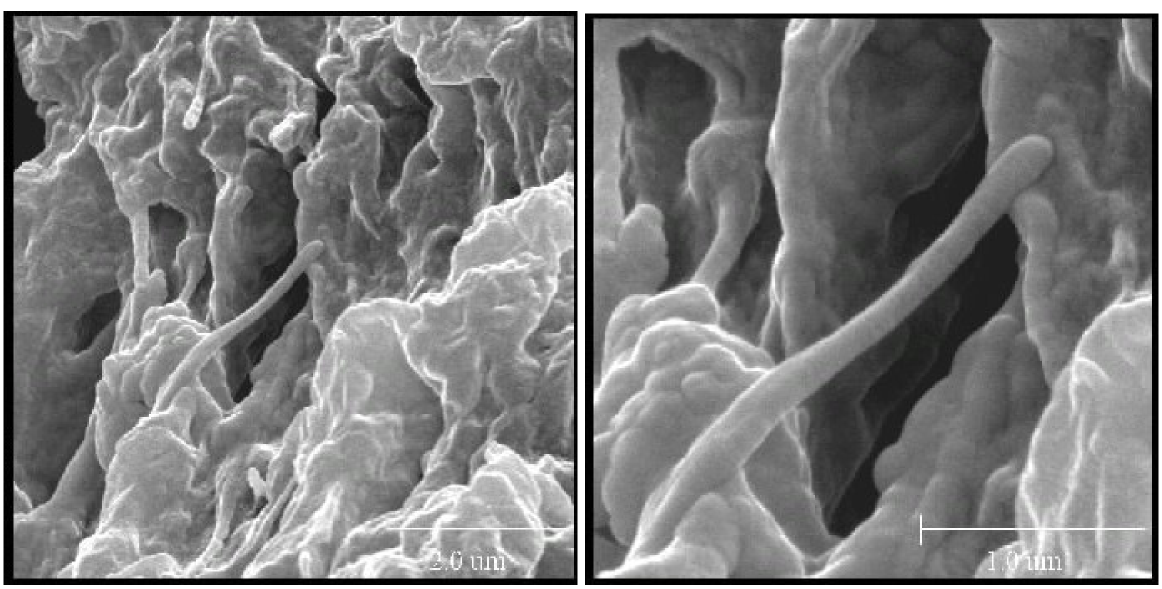
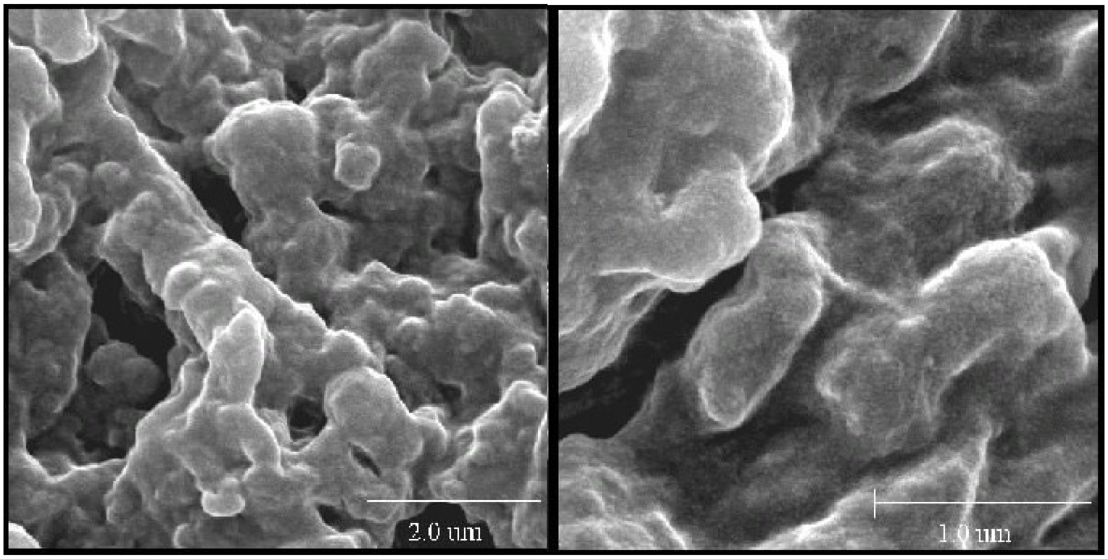


Figure 15: Aluminum Complex Grease made in the STRATCO® Contactor™ Reactor

20,000 X **50,000 X**



Summary and Conclusions

Regarding simple lithium greases, the micrographs indicate that well developed fiber structures of a similar nature can be produced using all three types of batch reactors. The commercial samples in this study revealed that the autoclave sample was composed of generally thinner fibers than that of the other two methods while the Contactor reactor sample was generally thickest. However, it must be recognized that the variations in processing (e. g., maximum reaction temperature, heating rate, cooling rate, milling/homogenizing, etc.) could affect fiber structure. Consequently, it cannot be assumed that thinner fibers are universally produced in all autoclave processes. It can also be said that greases manufactured on a lab scale seem to be similar to commercial products with respect to structure and properties. Such similarities are evident with significant differences in processing time, both on a commercial scale (3 to 4 hours vs. 5 to 6 hours vs.

8 to 10 hours for Contactor reactor, autoclave and open kettle, respectively) and on a laboratory scale (4 hours vs. 10 hours for Contactor reactor and open kettle).

Regarding lithium complex, the micrographs indicated that the autoclave structure was unique, while the commercial greases produced in the Contactor reactor and open kettle appeared similar to each other. The autoclave grease appeared to be formed predominantly of straighter fibers compared to the other two methods, which included more fibers of a spiral nature. The micrographs of the autoclave grease appeared to show a film-like secondary structure, which was not apparent in the other two samples. Although this would be assumed to be related to the complexing agent, the dropping points of the three samples suggest clearly that all were complex greases. Additionally, as with the simple lithium greases, the greases from all three methods indicate the formation of well-developed fiber structures. Also, our samples revealed the Contactor reactor sample to possess generally thicker fibers. The quality of the fiber structure is not diminished by the significant reduction in processing time associated with the Contactor reactor.

Regarding anhydrous calcium grease, the micrographic comparison is only valid between the Contactor reactor and the open kettle. Our samples indicate that good quality fiber structures are produced with both of these methods. However, again the Contactor reactor sample appears to be formed of generally thicker fibers.

With respect to aluminum complex grease, the microscopic structure does not appear as individualized fibers. The autoclave grease has a smoother surface texture than the Contactor reactor grease. This may offer the ability to hold a greater volume of lubricating oil with less thickener.

In all cases, the micrographic comparison has shown that the manufacture of greases in the Contactor reactor, with its inherent high shear blending and rapid heat transfer and reaction time, does not sacrifice the integrity of grease structure. In fact, the samples evaluated in this study indicate that the use of the Contactor reactor results in generally thicker grease fibers. This holds true even though processing time is 30% to 50% less than with the other two methods and with a lower soap content.

Acknowledgements

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