

EVALUATION OF VARIOUS RAW MATERIAL OPTIONS FOR PRODUCING ALUMINUM COMPLEX GREASES

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Abstract

Aluminum complex greases represent a high performance grease type with specialized applications, which is steadily growing in widespread markets. Several options are available to the grease manufacturer regarding raw materials and manufacturing methods. One alternative Aluminum compound is Aluminum Isopropoxide (AIP). This is a single Aluminum atom with three isopropylate groups attached. When making grease with this reactant, isopropyl alcohol is liberated from the reaction. Another alternative compound, which is widely used, is a cyclic trimer of Aluminum. This is a ring structure containing three reactive Aluminum atoms connected by three Oxygens. The Aluminum atoms have an alcohol attached to them as well, which will liberate in the saponification reaction. The most recent alternative is a structure very similar to a cyclic trimer with a fatty acid reacted with it. Only portions of both acids need to be added to this almost preformed soap, from which isopropyl alcohol has already been removed. The price of these three alternative Aluminum compounds increase from AIP, cyclic trimer to the preformed soap, respectively. A lab scale STRATCO® Contactor™ reactor was used to make Aluminum complex greases using the three mentioned reactants. Holding the base oil type, soap concentration and reaction parameters constant, the physical properties are analyzed and compared.

Introduction

Aluminum complex (AIX) greases represent a significant segment of the worldwide grease market. According to the NLGI Grease Production Survey issued in June 2004¹, in calendar year 2003 of the companies surveyed, over 37,428 metric tonnes of AIX grease were produced worldwide. In terms of market share of complex greases, it was second only to Lithium complex grease. Whereas it represented 4.9% of the total world grease market, it represented approximately 8.8% and 5.6% of the North American and European grease markets, respectively. The desirable properties associated with this grease type, including high dropping point, water resistance, low oil separation, mechanical stability and pumpability, contribute to its suitability in a variety of specialized applications, as well as its approval for food manufacturing applications.

In consideration of its growth in the world market, the variety of raw material options in its manufacture and the variety of production methods, the authors felt it very worthwhile to explore the various raw material options and compare the end products qualitatively, while observing any differences and/or difficulties in processing. Although AIX greases have been commercially produced using the Contactor reactor as early as the 1960's, the majority of AIX greases today are manufactured using conventional atmospheric kettles or autoclaves. Whereas a batch of AIX grease can be produced in four hours using a Contactor reactor², it is not uncommon for batches produced by conventional means to require in excess of 20 hours. Since it has been established that a good quality commercial AIX grease is produced in the Contactor reactor, the focus of this study was to compare the products resulting from the various raw material options using: (1) cone penetration, (2) dropping point, (3) Storage Modulus, (4) Loss Modulus, (5) Creep and (6) Yield with items (3) through (6) measured with a rotational disc rheometer. The raw material options used in this study were as follows:

1. Cyclic Trimer (Manufacturer A)
2. Cyclic Trimer (Manufacturer B)
3. Preformed Soap (Manufacturer B)
4. Preformed Soap (Manufacturer A)
5. AIP (Manufacturer A)

Each of the above result in the formation of an aluminum benzoate stearate soap thickener, but the manufacturing processes differ significantly between the three raw material options. AIP is a linear molecule, which requires water to finish the reaction. The cyclic trimer does not require the addition of water and produces one third of the isopropyl alcohol (a reaction byproduct) compared to the AIP. The preformed soaps are produced by reacting the trimer with a sufficient amount of stearic acid to evolve all of the alcohol, thereby eliminating this byproduct from the grease manufacturer's operations. Obviously, with both stearic and benzoic acid included in the preformed soap, less acids and base oils will be added during the manufacturing process. However, the mass of the preformed soap will be greater than the mass of the AIP or trimer by this same difference in mass.

Equipment and Procedures

The equipment used for this project included the following:

1. STRATCO® Model VJS 8-12.5-17.2 Contactor™ reactor
2. Groen Model NSP Double-Motion kettle
3. Viking Model H32 gear pump
4. Cuno Auto-Klean filter (0.005 in. spacing)
5. Chemicolloid Labs Model G-5 mill

Figure 1 provides a picture of the equipment configuration.



Figure 1. Equipment Arrangement

The general procedure was to perform the reaction phase in the Contactor reactor and then manually transfer the product to the finishing kettle. The procedures varied in the reaction phase with the different raw materials. The product was recirculated through the mill with the rotor retracted and motor off, through the filter and back to the kettle to facilitate cooling. When suitably cooled, the circulation was stopped, the mill set at 5 microns and energized and milling performed prior to drawing samples. The first product was milled at 10 microns as well as 5 microns. As the dropping points and penetration remained the same for both settings, the gap setting was limited to 5 microns for the remainder of the tests.

The base oil used was a blend of paraffinic and naphthenic base stock with an aromatic content of less than 1% by weight. The properties are presented in Table 1. Although the aniline point was not given by the manufacturer, the low aromatic content should result in a fairly high value, which generally would require a benzoic to fatty acid (B/F) ratio of less than one. Our experiments utilized an acid ratio of 0.75 for all products.

API Base Stock Category	Group II
API Gravity, ASTM D 1298	30.4
Specific Gravity at 15.5°C (60°F)	0.874
Kinematic Viscosity, ASTM D 445	
cSt at 40°C	116
cSt at 100°C	12.5
Saybolt Viscosity, ASTM D 2161	
SUS at 100°C	604
Viscosity Index, ASTM D 2270	98
Pour Point, °C(°F), ASTM D 97	-12 (+10)
Flash Point, COC, °C(°F), ASTM D 92	270 (518)
Carbon Type by n-d-M, ASTM D 3238	
% Paraffinic	72
% Naphthenic	28
% Aromatic	<1

Table 1. Base Oil Specifications

Both manufacturers supplying raw materials for this study provide technical support for their product lines. The procedures followed for each product were generally in accordance with the recommendations of the manufacturer. The material balances were adjusted such that all products had the same soap content, which was 9% by weight. As the focus of this study was primarily focused on comparing basic structure, no additives were used. The general procedure using the trimers or the preformed soaps was as follows:

1. Charge base oil. Heat to 100°C.
2. Add trimer/soap and stearic acid and allow to melt/react.
3. Cool to 93°C. Add benzoic acid.
4. Heat to 200°C.
5. Manually transfer to finishing kettle.
6. Recirculate and cool to 135°C
7. Mill at 5 micron gap setting

The procedure using AIP is very similar to the procedure described above, with the exception of addition of water after the addition of the benzoic acid. The water was added very slowly to avoid excessive thickening. (The first AIP batch produced in this study solidified almost instantly when water was added too quickly.) Other precautions include the order of addition of the acids and the temperatures during those additions. Although some literature might indicate adding both acids initially, our study confirmed that the best results will be obtained by allowing the stearic acid to melt and react with the aluminum compound prior to adding the benzoic acid. Furthermore, the temperature is recommended to be between 90°C and 95°C to avoid sublimation at higher temperatures and undesirable insoluble byproducts at lower temperatures. The B/F ratio can be varied to adjust thickening efficiency and dropping point due to variations in aniline point of base oils, but this tends to reduce mechanical stability. However, the total acid to aluminum ratio (approximately 1.9 in this study) can also be varied to offset reductions in mechanical stability. Such ratio adjustments are not addressed in this study.

Care was taken in flushing both vessels and piping between product types to minimize "contamination". Flushing was performed with base oil heated in the Contactor reactor, which was the same base oil that was used in the products. The filter was also disassembled and cleansed after each production run.

Experimental Results and Data

The products that are the subject of this study will be referenced as Sample #1 through Sample #5, which correspond to the list presented in the Introduction of this paper. Temperature vs. Time plots for the reaction phase were generated for each sample, shown here in Figures 2 through 6. Cooling rates in the finishing kettle were approximately the same for all products, the rate being about 2.8°C/minute. Milling was performed after the product temperature reached 137°C in the kettle.

Time Vs. Product and Heat Transfer Oil Temperatures (C)

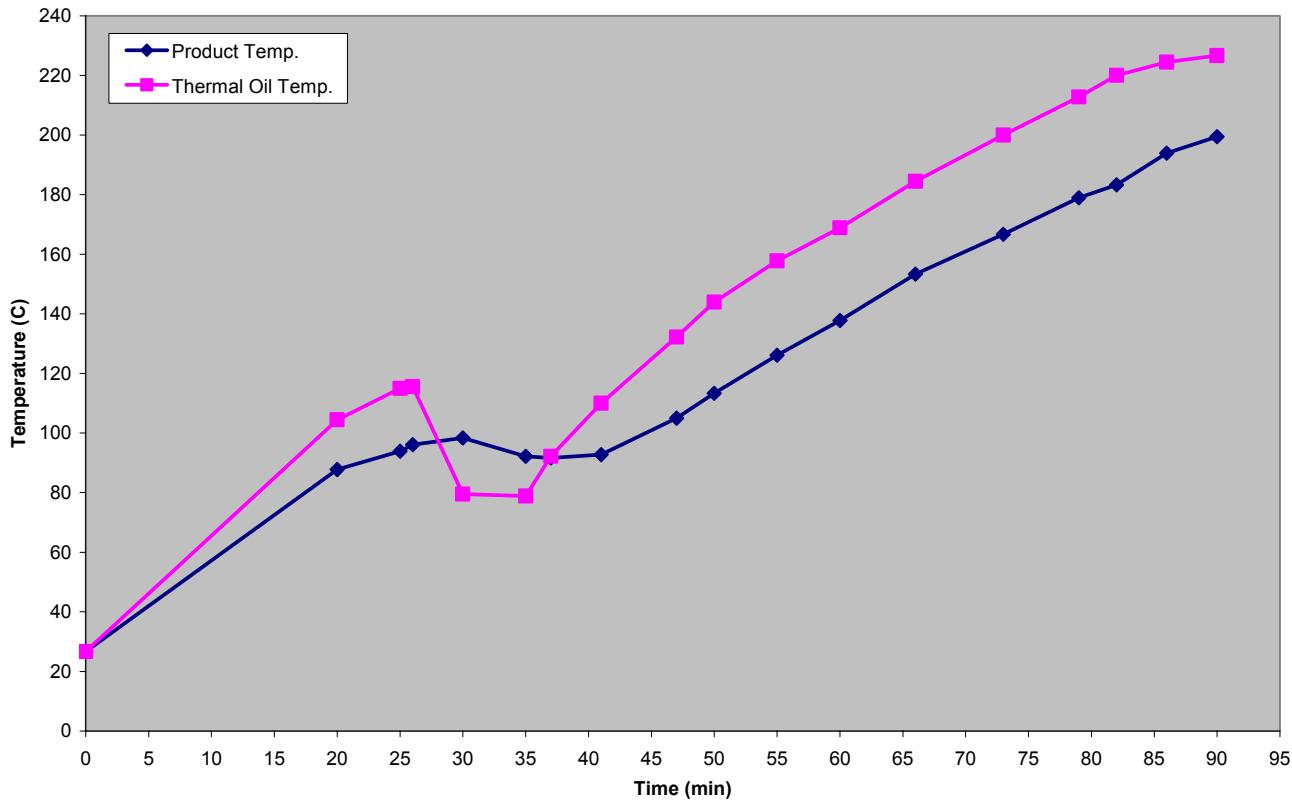


Figure 2. Temperature vs. Time Plot (Sample #1 Manufacturer A Trimer)

Time Vs. Product and Heat Transfer Oil Temperatures (C)

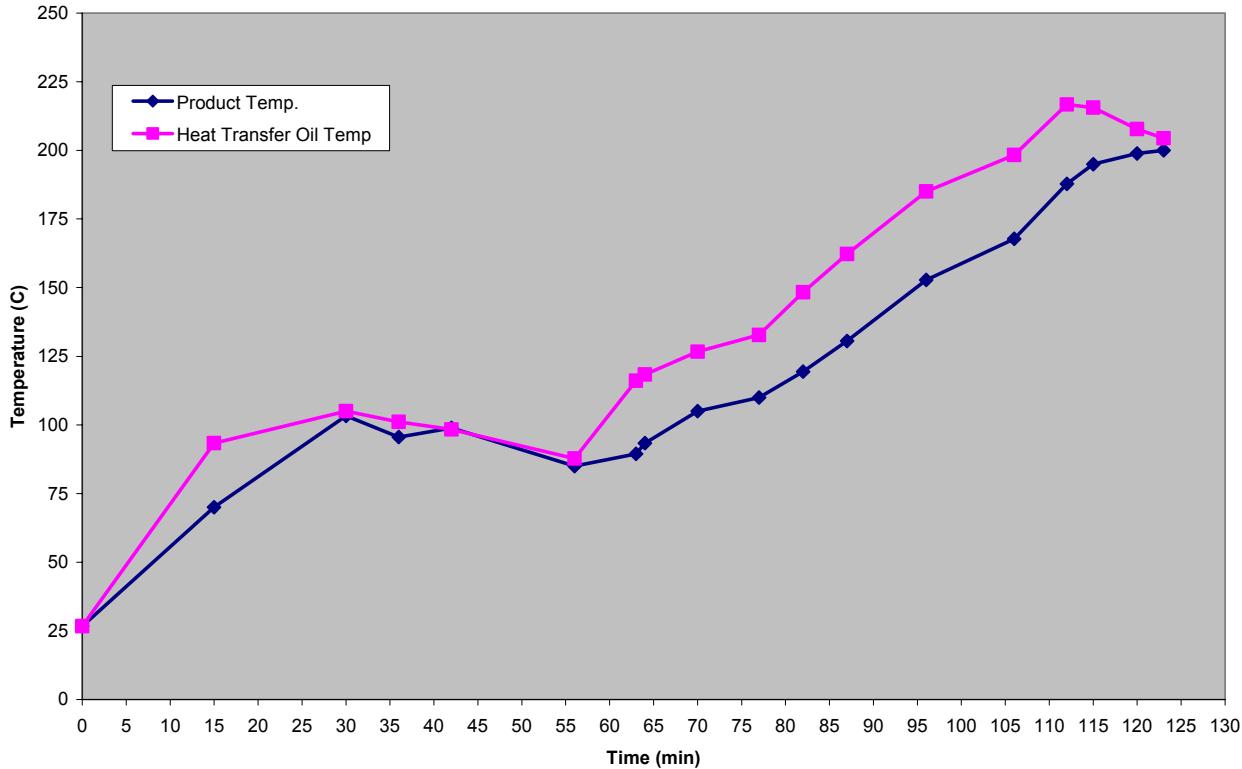


Figure 3. Temperature vs. Time Plot (Sample #2 Manufacturer B Trimer)

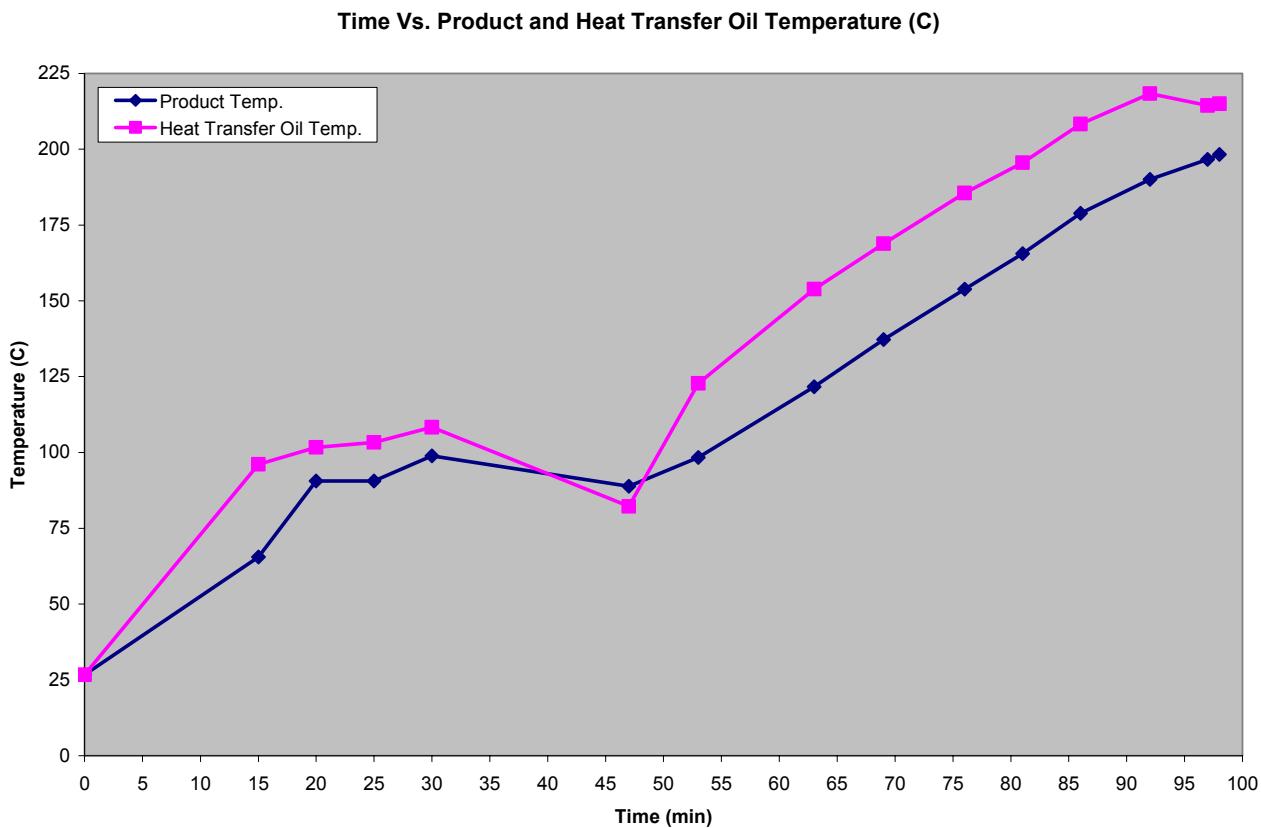


Figure 4. Temperature vs. Time Plot (Sample #3 Manufacturer B Preformed Soap)

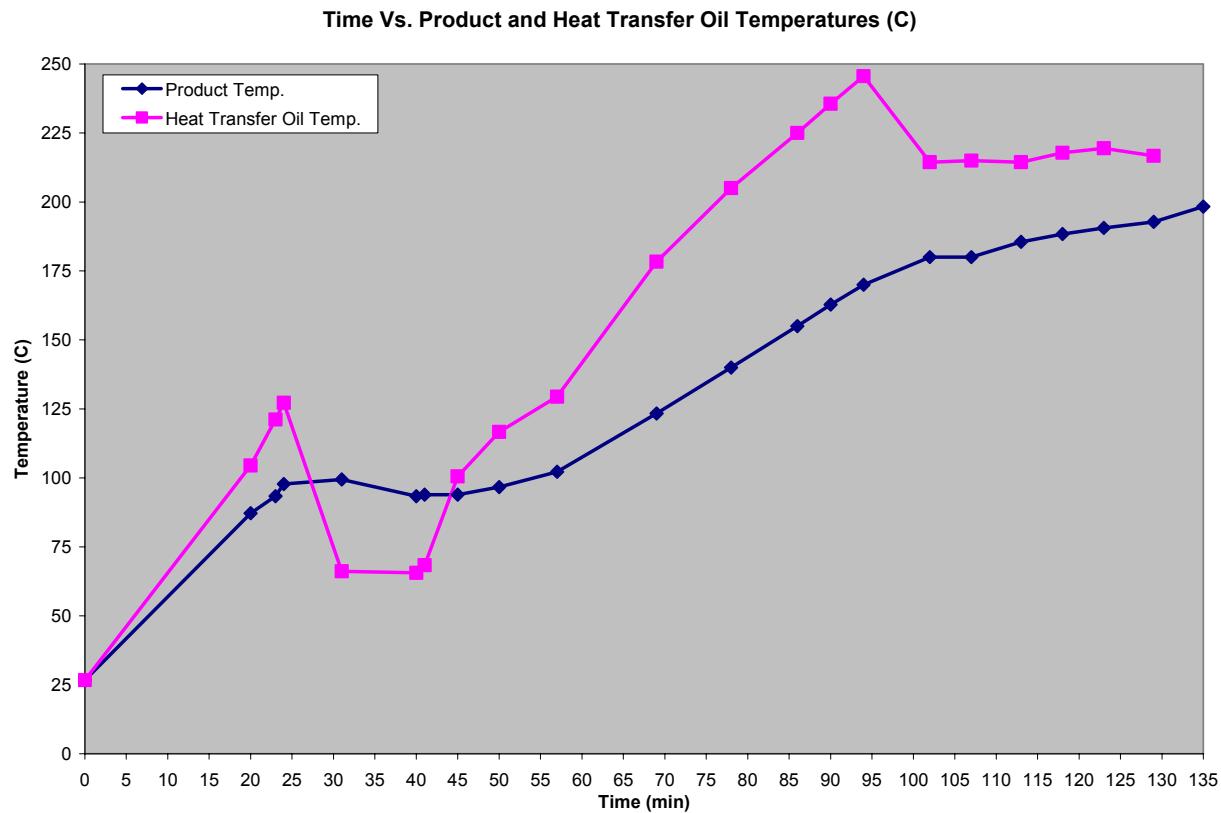


Figure 5. Temperature vs. Time Plot (Sample #4 Manufacturer A Preformed Soap)

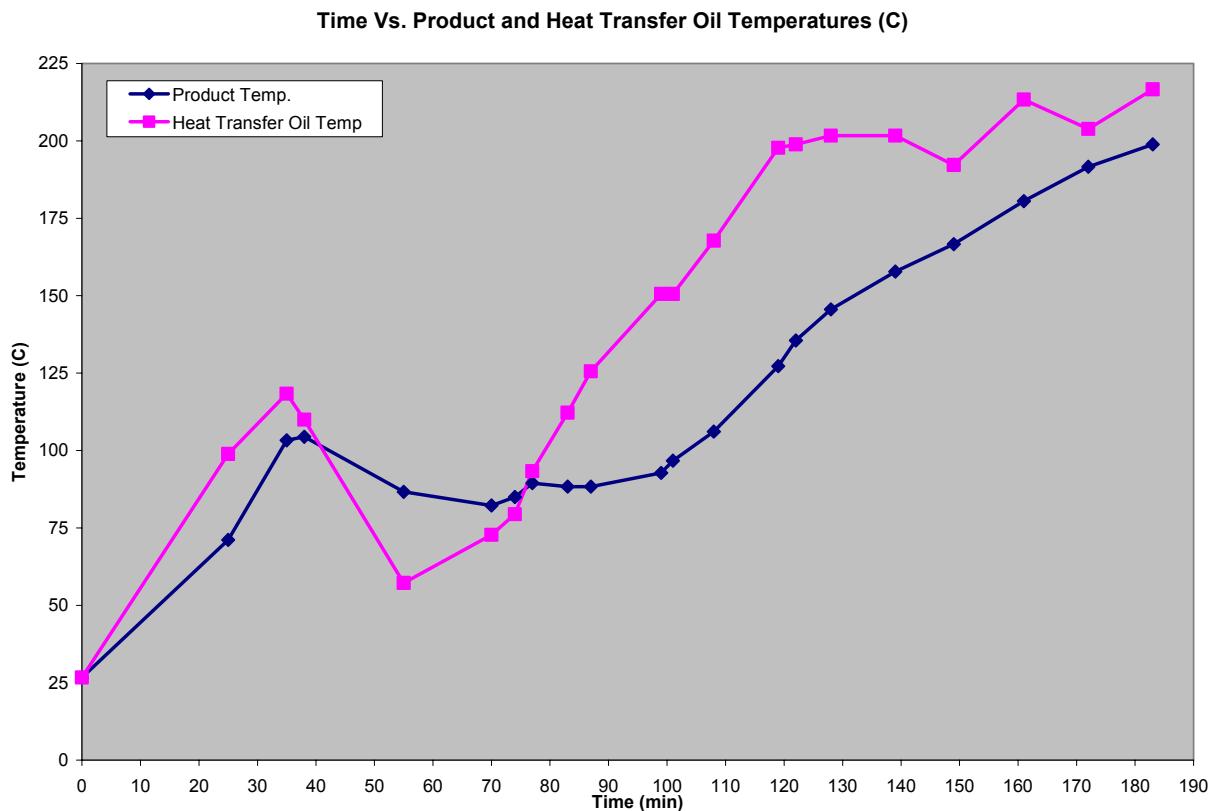


Figure 6. Temperature vs. Time Plot (Sample #5 Manufacturer A AIP)

Considering that a picture is worth a thousand words, Figure 7 is offered as a visual comparison of the five product samples. Initial measurements taken were of dropping points and cone penetrations. These are presented in Table 2. Additionally, in consideration of the concern of age hardening for this grease type, additional unworked cone penetration measurements were taken for comparison. These measurements are presented in Table 3.

Furthermore, in consideration of the recent trend to evaluate greases using rheometers in lieu of simple cone penetration³, the samples were analyzed with this method. A TA Instruments Model AR-1000 Rheometer was used, with all tests at 25°C. A 4 cm diameter 2° cone was used. The Storage Modulus (G') and Loss Modulus (G'') are plotted in Figures 8 and 9, respectively, using an oscillatory frequency of 1 Hertz. Creep and Tan Delta (G''/G') are plotted in Figures 10 and 11, respectively. The creep test was performed at 100 Pa. Yield is plotted in Figure 12.



Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
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Figure 7. Aluminum Complex Grease Samples

Test Description	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Dropping Point, ASTM D 2265, °C	252.8	252.8	252.2	253.9	255.0
Cone Penetration, ASTM D 217					
Unworked	281	290	288	277	281
Worked (60 stroke)	298	305	294	295	290

Table 2. Dropping Points and Penetrations

Days Elapsed	Sample 2	Sample 3	Sample 4	Sample 5
0	290	288	277	281
1		280	280	
2	297			
7				261
8		276	269	
9	280			
14				252
15		271	257	
16	272			
18				255
19		268	260	253
20	267	267	260	
21	265			
24				255
25		261	255	
26	266			

Table 3. Unworked Penetrations (Age Hardening)

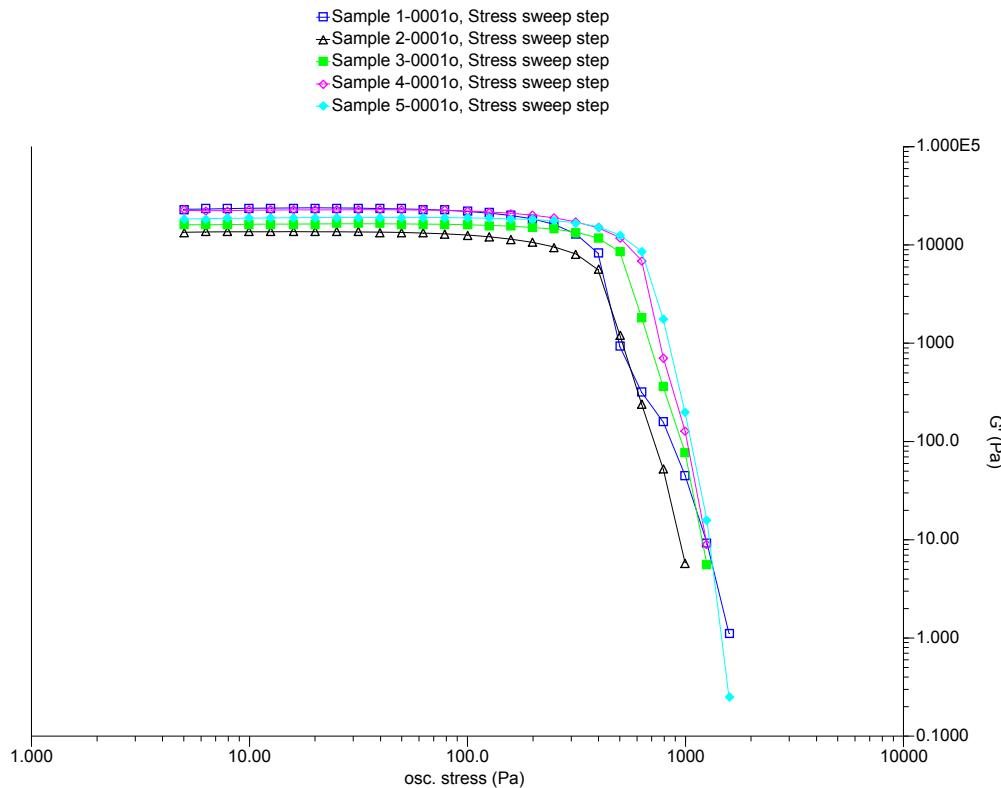


Figure 8. Storage Modulus Plot

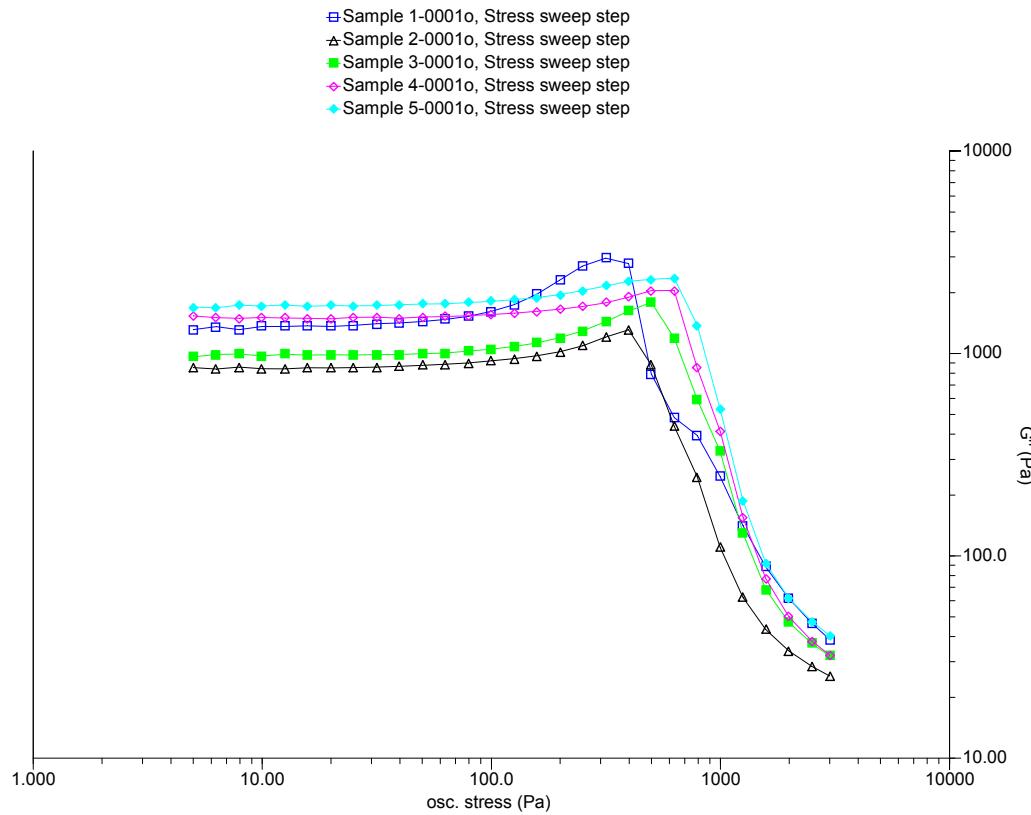


Figure 9. Loss Modulus Plot

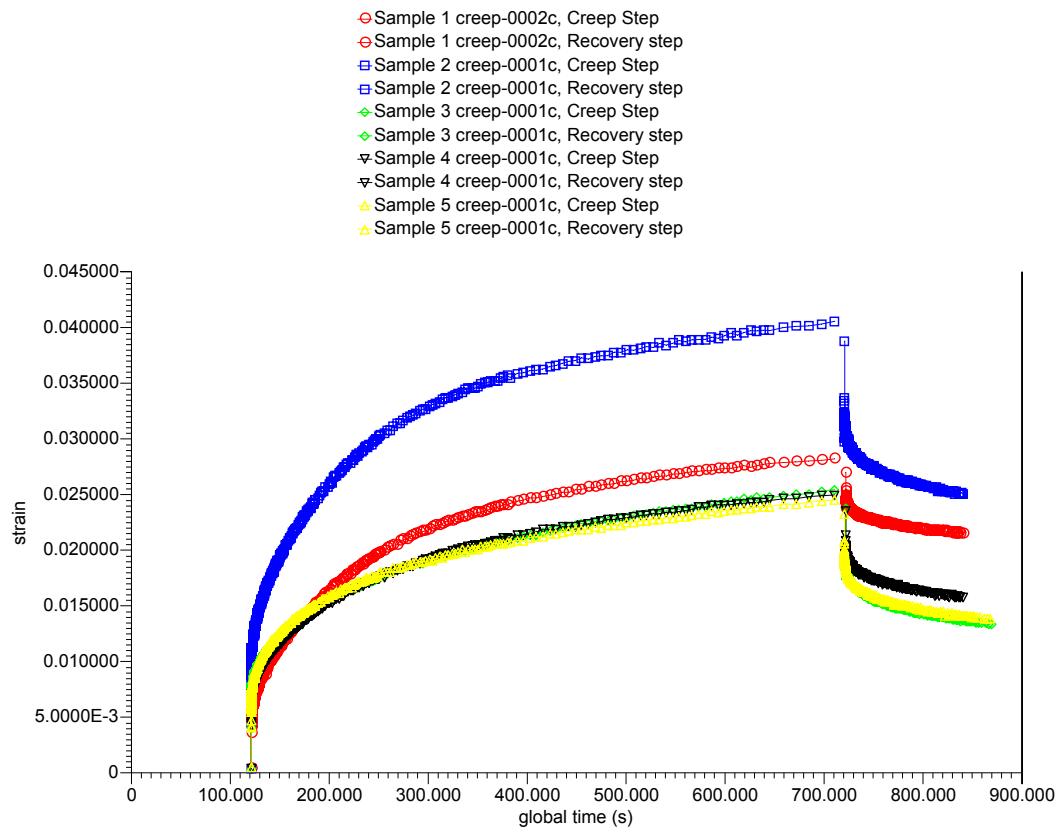


Figure 10. Creep Plot

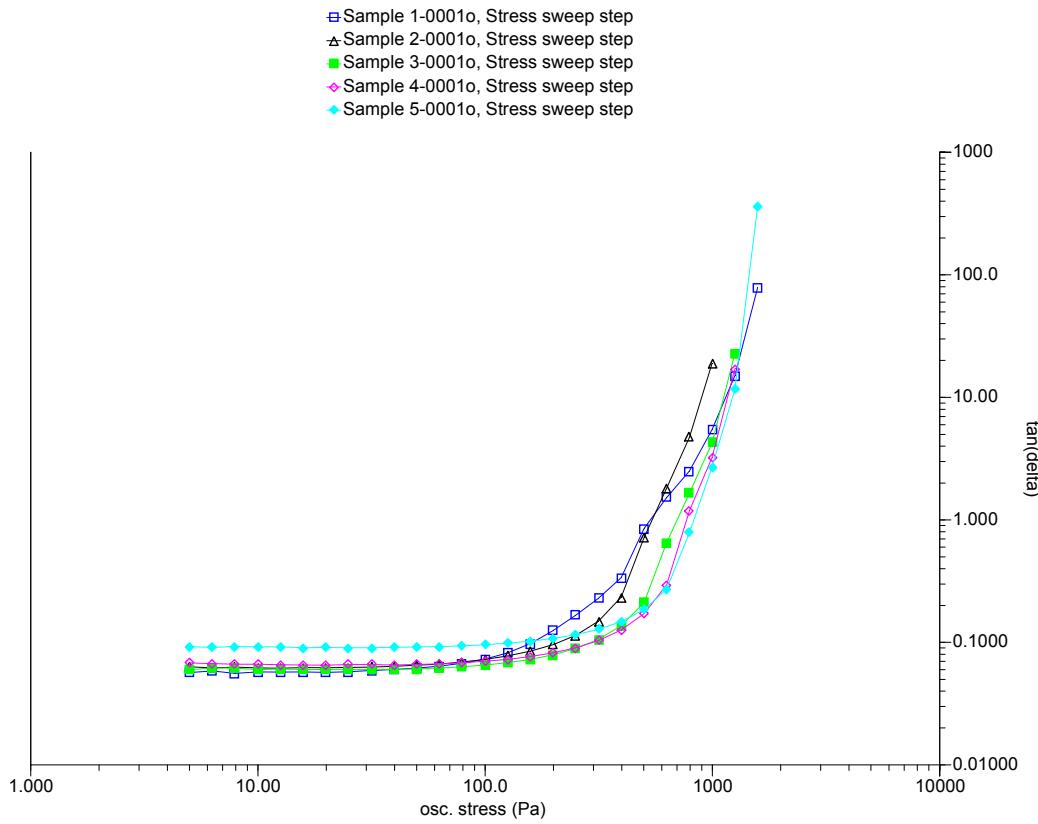


Figure 11. Tan Delta (G''/G') Plot

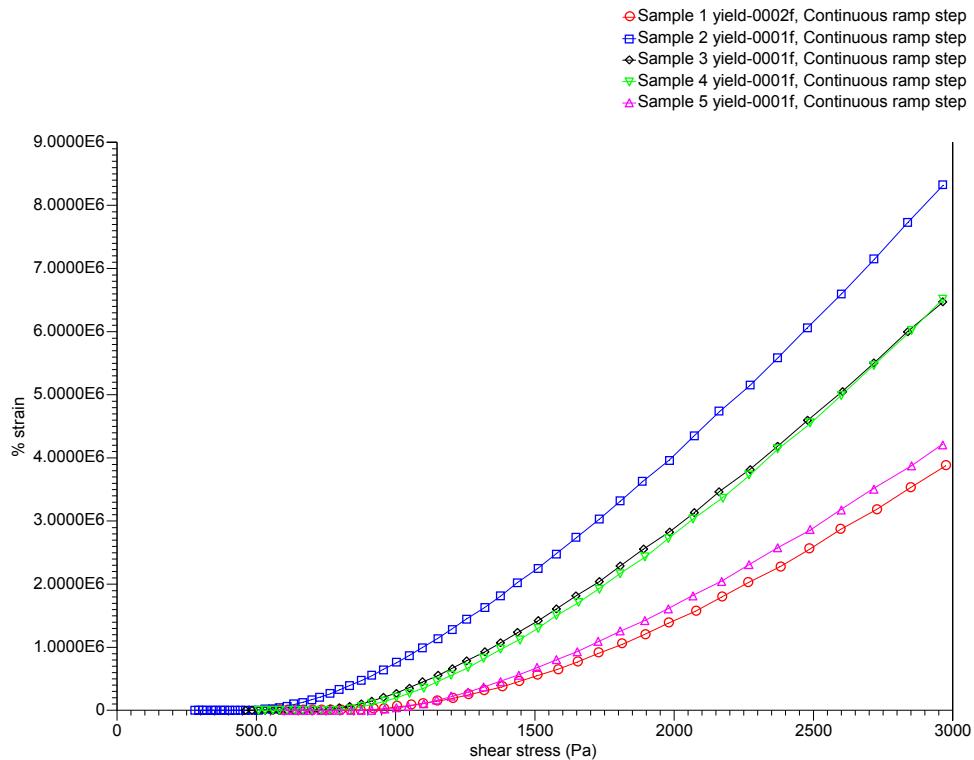


Figure 12. Yield Plot

Analysis and Conclusions

In terms of simplicity of production, the most difficulty was experienced with the AIP, specifically with the controlled addition of the water. When added quickly, thickening was almost instantaneous, which could be due to the highly efficient dispersion resulting from the Contactor reactor's internal recirculation. This gelling reduced the internal circulation and, consequently, the heat transfer to the product, which resulted in the increased heating time of about 180 minutes compared to the 90 to 135 minutes experienced with the other products. However, it is worthwhile noting that the clearances and flow in a commercial scale reactor should not experience such a significant increase in reaction time, as documented in previous studies of commercial production using AIP⁴.

It is also worthwhile noting that our laboratory heating system regulates the heating of the reactor by varying the thermal oil temperature, which suits our needs very well. However, on a commercial scale, the recommended practice is to maintain the thermal oil at its maximum supply temperature. Reactor temperature regulation is best controlled by mixing the supply stream to the reactor with the return stream and only cooling a fully recirculated stream. This allows you to access the primary supply stream at its maximum temperature at any time and you are not limited by the time necessary to reheat the entire system.

As mentioned previously, temperature control is very important to avoid undesirable effects with benzoic acid. The temperature control provided by the Contactor reactor is very accurate, with the temperature difference between the product and the heating medium maintained at a very controllable 30°C to 50°C. Also, the internal forced circulation ensures that the temperature through the vessel is within a degree or two of what is indicated by the temperature sensor.

All of the products were similar in appearance, which was smooth and translucent. All the dropping points were very close. Although these were slightly below 260°C, earlier “practice” batches with a different base oil resulted in dropping points above 260°C. Adjusting the B/F and TA/AI ratios could have been adjusted to optimize yield and dropping point, but could have significantly increased the duration of the study. Since our focus was a comparison of the different raw material options and not the optimization of each, we decided to postpone such investigations for a future study.

Due to the timing of the study, less than a month was available to monitor age hardening effects, although our plans are to continue gathering data after this paper is presented. Data was only monitored for Samples 2 through 5. Samples 2, 3 and 4 experienced decreases in penetration of about 10, 12 and 8, respectively, after one week, while Sample 5 had a decrease of 20. One week later, penetrations decreased an additional 8, 5, 12 and 9, respectively. Five days later, Samples 2 and 3 hardened by 7 and 4 points, respectively, while Samples 4 and 5 softened slightly. The samples in this study suggest that the trimer and preformed soap from Manufacturer B continue to show some hardening after three weeks, while both the preformed soap and AIP from manufacturer A appear to stabilize after three weeks. However, Sample 5 did experience the greatest degree of hardening of the four samples monitored. It was also interesting that Samples 2 and 4 exhibited an initial softening within the first couple of days, although that of Sample 4 was only slight. Obviously, further monitoring could reveal other trends that cannot be predicted at this time. Worked penetrations taken of Samples #1 through #5 after 24 days showed differences from the initial measurements of -5, -8, -7, -11 and -9, respectively.

An examination of the Loss Modulus (G'') plot (Figure 9) and the Storage Modulus (G') plot (Figure 8), which are representative of viscosity and elasticity, respectively, indicate the yield stress of each sample, at which points the G'' and G' begin to precipitously drop. The

yield stresses of Samples #1 through #5 are approximately 400 Pa, 400 Pa, 500 Pa, 610 Pa and 610 Pa, respectively. The “crossover point” referenced in ELGI’s Rheology text⁵, where G' is equal to G”, is shown in Figure 11 where Tan Delta equals 1.0. The “crossover points” for Samples #1 through Samples #5 are approximately 530 Pa, 530 Pa, 700 Pa, 780 Pa and 830 Pa, respectively. If this “crossover point” is considered to provide some additional value, it would suggest improved value of Sample #5 as compared to Sample #4, which was not so apparent in Figures 8 and 9.

The Loss Modulus values alone would indicate the order of improving quality (low to high) to be Samples #2, #3, #1, #4 and #5, assuming products of higher viscosity would maintain the same order of performance with increasing temperature. The Storage Modulus indicate the order of improving efficiency (low to high) to be Samples #2, #3, #5, #4 and #1, with the last two samples being almost identical numerically. In fact, numerically the efficiencies of all products are very close to one another.

Examining the creep data in Figure 10, Samples #3 through #5 behave very similarly, while Sample #1 is slightly worse and Sample #2 is noticeably the worst. Examining the Yield plot (Figure 12), the order of improving performance (low to high) is Sample #2, #3, #4, #1 and #5, two similar groupings comprised of #3/#4 and #1/#5. This plot was surprising in that other data seemed to associate # 1 with the #2, which exhibited the worst traits, while the Yield plot now associated it with #5, the sample generally exhibiting the highest qualities. It is interesting to note that, although both the G" and G' values for Sample #1 drop significantly at the same time as Sample #2, both curves offset after that point to closely coincide with the curves of Sample #5.

All the rheological data seem to suggest that the best properties are exhibited by Sample #5 and the worst are exhibited by Sample #2. However, Sample #5 also exhibited the highest degree of age hardening, although it had the lowest initial worked penetration. It is also worthwhile to note that this product was the only raw material without any carrier oil. Consequently, all the chemical interaction normally occurring between oil and thickener was completely determined by the formulator's base oil.

This study shows that rheological testing can differentiate between not only the three raw material options, but also similar material options from different manufacturers. This study also shows that general grease properties, such as dropping point and NLGI consistency, can be easily duplicated with any of the options using the Contactor reactor. The decision of which raw material option is most desirable for a grease manufacturer will be determined by cost, the capabilities of the process equipment and possible synergies with additive packages and their costs. The authors were advised that comparative costs on a per weight basis differed by approximately 15% to 20% between each of the three raw material options, i. e., from AIP to trimer to preformed soap. Operating conditions may, or may not, result in significant performance variation, but such comparisons would need to be verified empirically. It should also be recognized that the raw materials used in this study were from manufacturers historically recognized for high quality. Alternative sources of raw materials may result in lower quality finished products.

Acknowledgements

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Bibliography

1. NLGI Grease Production Survey Report for Calendar Years 2000 through 2003, June 2004.
2. Dreher, J. L., Koundakjian, T. H., and Carter, C. F., "Manufacture and Properties of Aluminum Complex Greases", *NLGI Spokesman*, July, 1965.
3. Johnson, B., "The use of a stress Rheometer in lieu of cone penetration", presented at ELGI 16th Annual General Meeting in Paris, 2004.
4. Dreher, Koundakjian, and Carter, p. 108.
5. Balan, C., ed., The Rheology of Lubricating Grease, ELGI, May, 2000, p. 63.