

Critical Variables in Lithium Complex Grease Manufacturing

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Abstract

Lithium complex greases represent a high performance grease type with specialized applications, and these greases are steadily growing in widespread markets. Several options are available to the grease manufacturer regarding raw materials and manufacturing methods. The selection of the complexing agent has economic ramifications and also performance and procedural considerations. Due to the differences in reactivity of the complexing agents, there may be optimum temperature profiles for each material. A lab scale STRATCO® Contactor™ reactor is used to make lithium complex greases using two common complexing agents, namely azelaic acid and sebacic acid. This type of reactor is used in order to have better control of the temperature profile during the process. Holding the base oil, soap concentrations (11%) and acid ratios (3:1) constant, the temperature profiles are varied and the physical properties are analyzed and compared to establish optimum reaction conditions.

Introduction

Greases made from Lithium possess many desirable properties, such as good water resistance, high temperature properties, shear resistance and pumpability as compared to other alkali metal based greases. Lithium complex grease is a great all-purpose lubricant because of its uses over a wide range of temperatures. According to a recent NLGI Production Survey, approximately 75 percent of the grease sold worldwide is based on either simple lithium soap or lithium complex thickener [1]. Lithium complex grease continues to slowly displace simple lithium grease because of its higher dropping point. This makes lithium complex ideal for higher temperature applications.

Lithium complex grease has a higher dropping point because of the presence of a complexing agent. Lithium complex grease is made with two molecules: the co-crystallization of a lithium soap molecule and a lithium dibasic salt molecule [2]. These dibasic salts are made by the saponification of a dicarboxylic acid with lithium hydroxide. Dicarboxylic acids have an acid functional group on both ends of the short-chain carbon molecule. Typical complexing agents are: azelaic acid, sebacic acid, adipic acid and sometimes boric acid [2]. Of these, azelaic acid and sebacic acid are the most widely used. The fluctuating raw material cost of these two chemicals can be a deciding factor on which complexing agent is used by a manufacturer. Due to the differences in reactivity of these two materials, it is important to recognize the differences in manufacturing processes inherent in each.

The general consensus, based on experience, regarding the strategy of reacting lithium complex greases is the need for allowing the initial simple saponification reaction to precede the reaction of the complexing agent. This is generally accomplished by maintaining the ingredients at a lower temperature range for a period of time to allow the simple reaction to be completed, followed by the elevation to the final reaction temperature. As with most grease manufacturing practices, procedures vary from manufacturer to manufacturer. The use of conventional kettles for the reaction stage

involves some inherent limitations of heating rates due to the heating surface available and the limited heat transfer rate associated with this type of vessel. The use of the pressure rated Contactor reactor allows faster heating and improved temperature control due to its greater heating surface and higher heating and cooling rates. The goal of this study is to determine the optimum heating profile and manufacturing practice using the Contactor reactor in order to achieve desirable properties with the limited residence time in the reactor. This will allow the manufacturer to produce this high performance product in the shortest time for a quicker turnover and the minimum lead time for their customer's product. Differences in manufacturing procedures include heating rates, holding times, the employment of a quench stage before transfer to the finishing kettle, and the consideration of a one-step versus two-step procedure.

The use of a quench stage in the Contactor reactor offers decidedly different conditions when compared to quenching, or cooling, in the finishing kettle, namely: (1) the quenching can be accomplished much quicker in the Contactor reactor and (2) the crystallized fibers will experience a higher shear in the Contactor reactor, resulting in a moderate milling effect. There is certainly a processing time advantage in having the base grease start at a lower temperature in the finishing kettle.

The strategy of a one-step versus two-step procedure represents a compromise between minimizing the manufacturing time and ensuring that the complexing reaction does not interfere with the simple reaction. The one-step method is characterized by the addition of all ingredients at the beginning of the reaction stage while the two-step method involves the addition of the complexing agent only after the simple reaction has been completed. Regarding the two-step method, the authors are aware of two different practices employed with the Contactor reactor: (1) cooling the Contactor reactor product after the simple reaction is completed and introducing the complexing agent for the balance of the reaction process in the Contactor reactor and (2) transferring the simple base grease and adding the complexing agent in the finishing kettle. This study will employ the former practice in order to minimize manufacturing time.

In summary, the key issues addressed in this study include:

1. Identifying the optimum intermediate temperature target representing the upper limit of the range of the simple reaction
2. Establishing the minimum time required in the simple reaction region
3. Establishing the minimum time required for the complex reaction
4. Determining the effects of quenching in the Contactor reactor
5. Verifying the need for a two-step process

Equipment and Procedures

Lithium complex grease batches were produced in the laboratory of Stratco, Inc. in Scottsdale, Arizona using a lab scale Stratco® Contactor™ reactor. Critical variables such as heating rates, intermediate temperatures, reaction times and quenching

techniques were studied through analysis of the batch properties. Properties evaluated were dropping point and penetration, including unworked, worked and 10,000 stroke. The dropping point was indicative of the quality of the complexing reaction while the penetrations were used to evaluate yield efficiency and mechanical stability.

In order to simplify the comparisons, a single, simple base oil was used, which was not specifically selected to optimize yield or dropping point. It was also decided to use the same soap content of 11% by weight for all the batches and not to use additives to avoid synergistic effects on the complexing agents. The acid ratios were also kept constant at 3:1 (12-HSA to complexing agents).

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, once transferred to the kettle, was recirculated by-passing the mill and filter to facilitate cooling. A portion of the base oil was withheld from the contactor and added to the kettle for cooling and dilution. When suitably cooled, the circulation was stopped, the mill set at 5 microns and energized and milling performed prior to drawing samples. All the batches throughout this study were quenched with a portion of base oil in the kettle and milled at 5 microns when the product dropped to 100°C for 10 minutes before taking samples.

The base oil used was a Group II 500 Neutral paraffinic oil. The other raw materials supplied were standard grade materials that are used in the grease industry. As mentioned previously, the additives were left out of the greases for this project to avoid synergistic effects with the chemically different complexing agents. The raw materials used were 12-hydroxystearic acid, lithium hydroxide monohydrate, azelaic acid and sebacic acid.

All batches started at 80°C after the initial ingredients were added and melted. They were then heated to an intermediate temperature over a specified period of time, then heated to 204°C to complete the complexing reaction, although one batch was allowed to reach 210°C. For the two-step method the batch was cooled from the intermediate temperature to below boiling temperature to add the complexing agent, then heated to 204°C. Although the water of reaction was vented to control the pressure at 5.5 bar, the residual water/steam was allowed to remain for the addition of the complexing agent in the two-step process in order to utilize the pressure when reheating to maintain flow and assist in the discharge. Several batches were allowed to cool (quench) in the Contactor reactor following the reactions, while the other batches were discharged and transferred immediately to the finishing kettle at the maximum reaction temperature. Based upon commercial experience, the target quench temperature was 182°C. Several of the sebacic acid trials were performed as a two-step process while all the others were a single step process. Quenching in the lab scale Contactor reactor was accomplished by cooling the thermal oil in the vessel jackets. In commercial operations, quenching is typically accomplished with the addition of base oil.

The variables manipulated were: heating rates between the beginning, intermediate and final temperatures, the intermediate temperature itself, as well as holding times at different temperatures. Charts 1 and 2 illustrate the test design and variable conditions for the two complexing agents.

| | | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Batch Number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Starting Temperature | 80°C |
| Ramp Time (min) | 60 | 35 | 60 | 47 | 35 | 60 | 25 | 25 |
| Intermediate Temperature | 150°C | 150°C | 150°C | 150°C | 150°C | 150°C | 130°C | 130°C |
| Hold Time | 0 | 0 | 0 | 0 | 0 | 0 | 35 | 10 |
| Ramp Time | 35 | 30 | 60 | 30 | 65 | 30 | 50 | 50 |
| Final Temperature | 204°C |
| Hold Time | 0 | 0 | 60 | 0 | 0 | 0 | 0 | 0 |
| Quench in Contactor Time | 0 | 0 | 0 | 0 | 0 | 25 | 25 | 25 |

Chart 1. Testing design conditions for azelaic acid

| | | | | | | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Batch Number | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Starting Temperature | 80°C |
| Ramp Time (min) | 60 | 35 | 60 | 60 | 60 | 25 | 25 | 15 | 15 | 15 | 25 | 20 |
| Intermediate Temperature | 150°C | 150°C | 150°C | 150°C | 135°C | 130°C | 130°C | 130°C | 121°C | 121°C | 130°C | 130°C |
| Hold Time | 0 | 0 | 0 | 0 | 0 | 35 | 35 | 45 | 15 | 15 | 35 | 10 |
| Ramp Time | 60 | 35 | 35 | 35 | 35 | 65 | 65 | 50 | 50 | 50 | 65 | 65 |
| Final Temperature | 204°C | 204°C | 204°C | 204°C | 204°C | 210°C | 204°C | 204°C | 204°C | 204°C | 204°C | 204°C |
| Hold Time | 60 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Quench in Contactor Time | 0 | 0 | 0 | 25 | 25 | 0 | 0 | 0 | 0 | 25 | 25 | 0 |

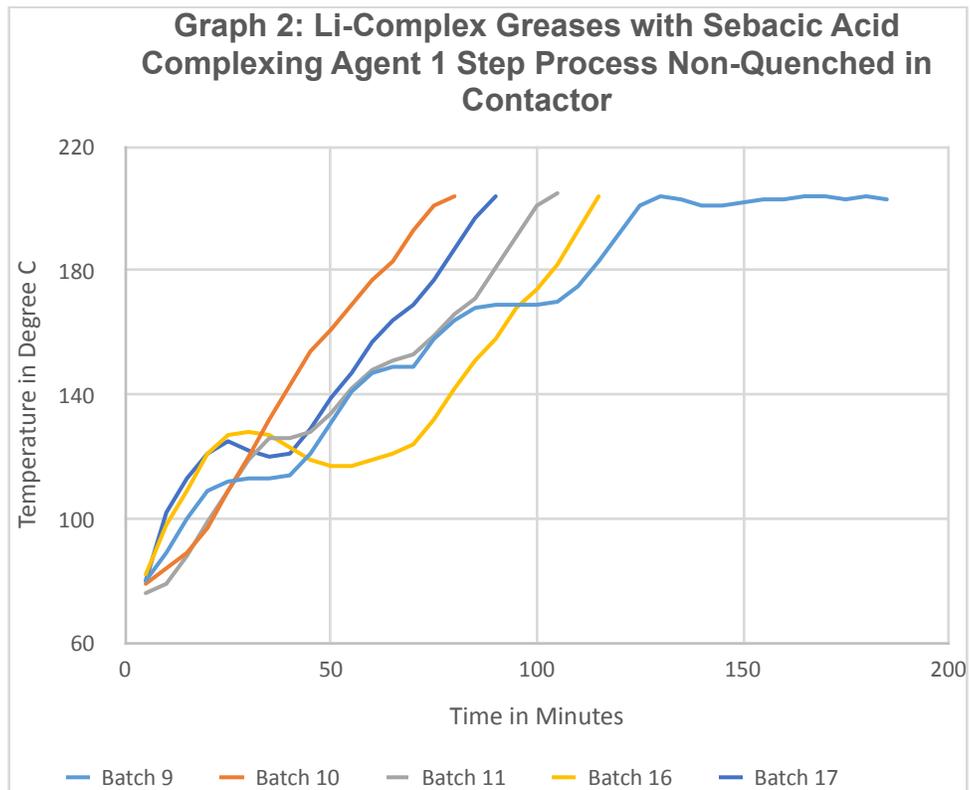
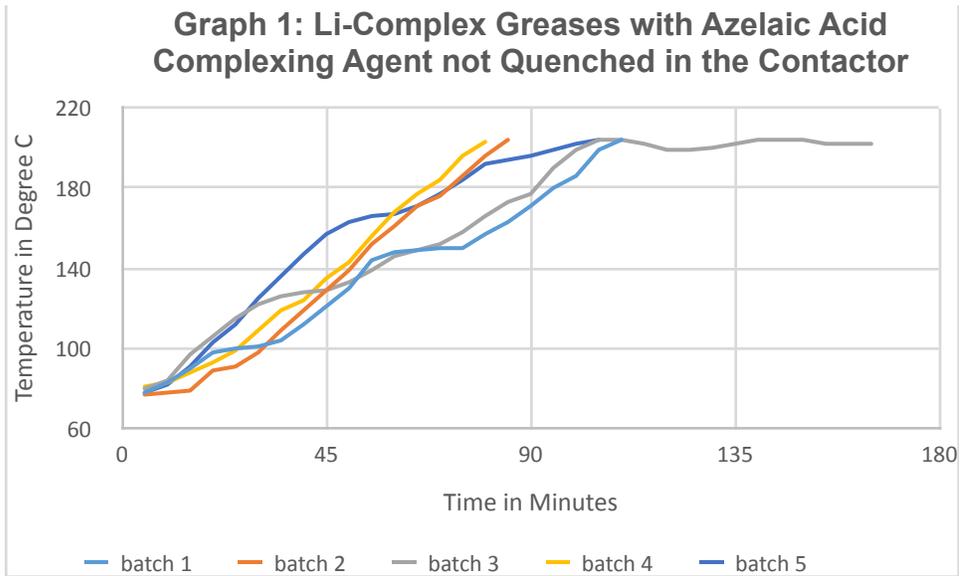
Highlighted batches used the two-step process

Chart 2. Testing design conditions for Sebacic Acid

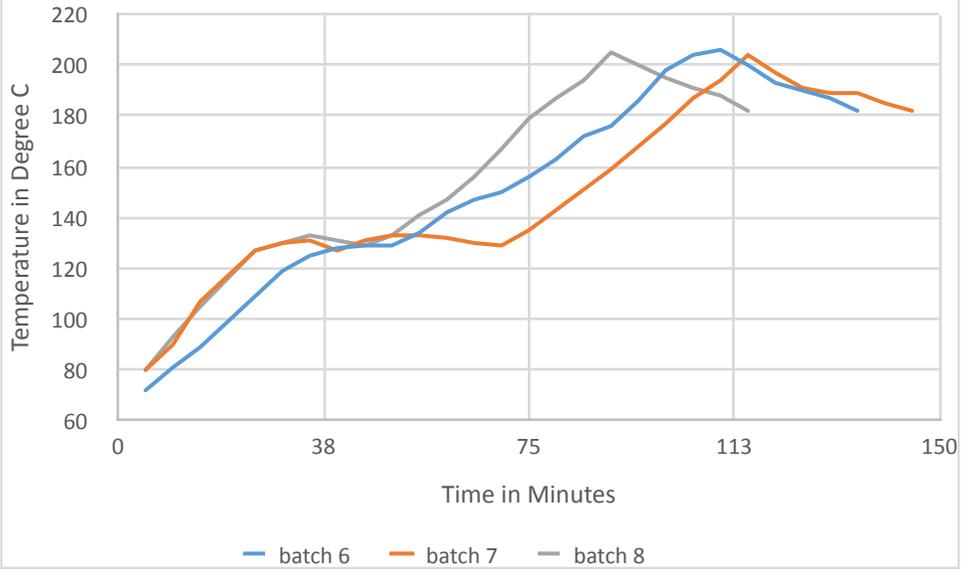
Experimental Results and Data

The greases were made in the Contactor reactor starting with the azelaic acid complexing agent then moving on to the sebacic acid complexing agent. Data recorded included product temperature, thermal oil supply temperature, vessel pressure and motor amperage versus time. Motor amperage remained steady throughout testing.

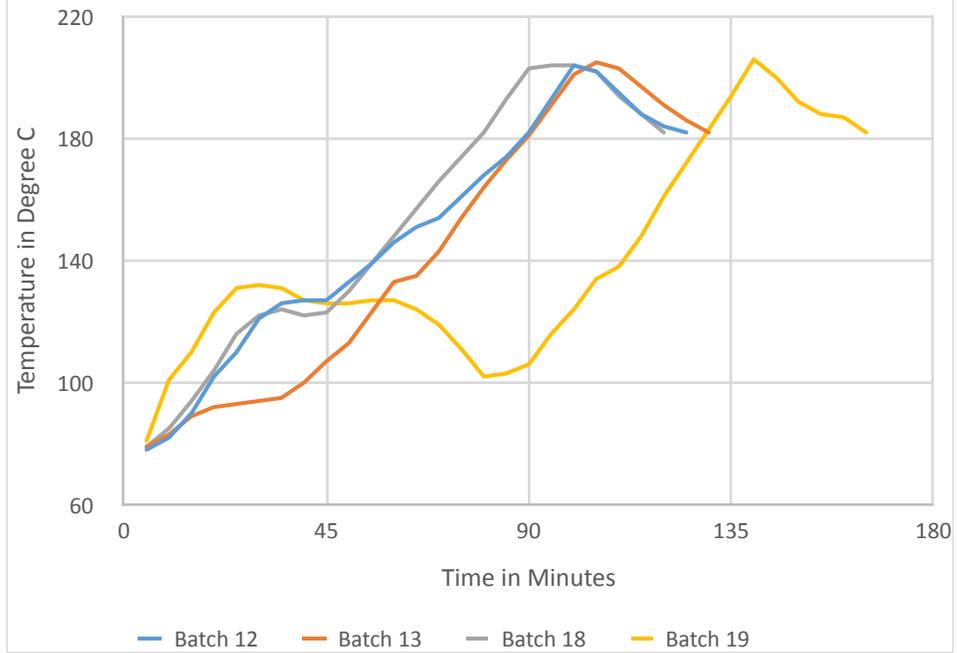
Time vs. Temperature plots were generated for all batches, which are shown in Graphs 1 through 5.

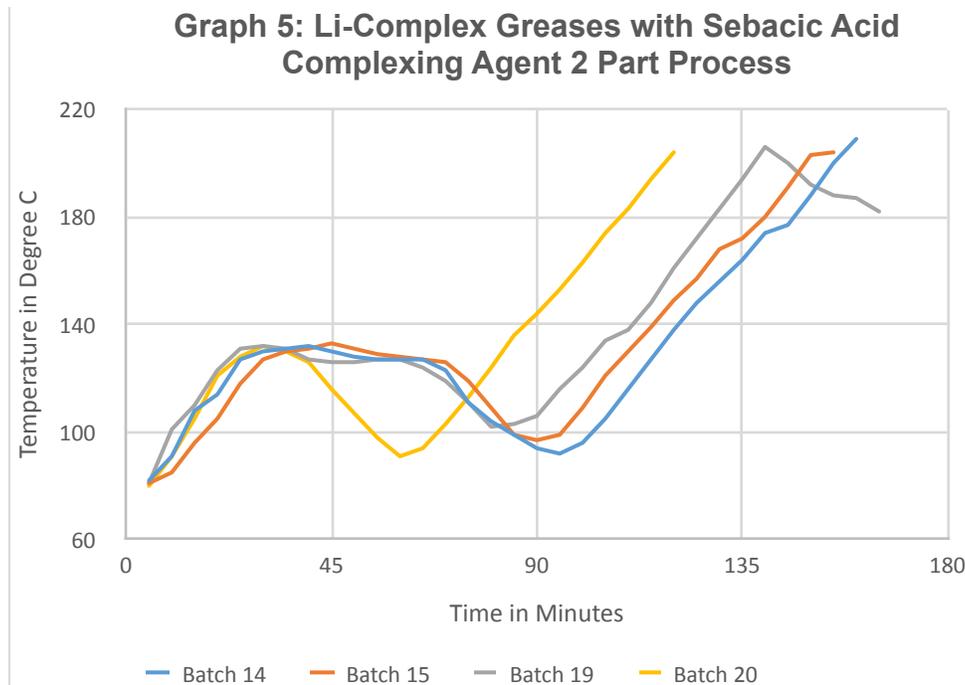


Graph 3: Li-Complex Greases with Azelaic Acid Complexing Agent Quenched in Contactor



Graph 4: Li-Complex Greases with Sebacic Acid Complexing Agent Quenched in Contactor





The grease batches were tested for unworked penetration, 60 stroke penetration, as well as 10,000 stroke penetration. These tests were performed in accordance with Cone Penetration ASTM D 217. Dropping points were also determined using standardized test ASTM D 2265, °C. Charts 3 and 4 show the results of the aforementioned tests. Chart 5 summarizes total residence time in the Contactor reactor for all test batches, including charging time.

| Batch | Unworked Penetration | 60 Strokes Penetration | 10,000 Strokes Penetration | Difference 60 vs 10K | Dropping Point°C |
|-------|----------------------|------------------------|----------------------------|----------------------|------------------|
| 1 | 287 | 292 | 339 | 47 | 250 |
| 2 | 318 | 329 | 381 | 52 | 232 |
| 3 | 294 | 313 | 349 | 36 | 250 |
| 4 | 322 | 318 | 377 | 59 | 226 |
| 5 | 294 | 304 | 338 | 34 | 257 |
| 6 | 279 | 286 | 309 | 23 | 262 |
| 7 | 274 | 279 | 304 | 25 | 263 |
| 8 | 268 | 278 | 364 | 86 | 243 |

Chart 3. Test results for azelaic acid complexing agent

| Batch | Unworked Pennetration | 60 Strokes Pennetration | 10,000 Strokes Pennetration | Difference 60 vs 10K | Dropping Point°C |
|-------|--------------------------|----------------------------|--------------------------------|-------------------------|---------------------|
| 9 | 309 | 311 | 351 | 40 | 211 |
| 10 | 301 | 298 | 378 | 80 | 212 |
| 11 | 278 | 294 | 381 | 87 | 235 |
| 12 | 267 | 262 | 383 | 121 | 232 |
| 13 | 281 | 265 | 379 | 114 | 223 |
| 14 | 271 | 272 | 284 | 12 | 263 |
| 15 | 273 | 262 | 279 | 17 | 265 |
| 16 | 280 | 280 | 295 | 15 | 246 |
| 17 | 278 | 280 | 302 | 22 | 251 |
| 18 | 273 | 263 | 338 | 75 | 218 |
| 19 | 268 | 265 | 280 | 15 | 258 |
| 20 | 279 | 273 | 281 | 8 | 272 |

Highlighted Batches used the two-step process

Chart 4. Test results for sebacic acid complexing agent

| Batch | Hours | Minutes | Batch | Hours | Minutes |
|-----------|----------|-----------|-----------|----------|-----------|
| 1 | 1 | 30 | 11 | 1 | 40 |
| 2 | 1 | 10 | 12 | 2 | 0 |
| 3 | 3 | 0 | 13 | 2 | 0 |
| 4 | 1 | 15 | 14 | 2 | 30 |
| 5 | 1 | 40 | 15 | 2 | 21 |
| 6 | 2 | 0 | 16 | 1 | 50 |
| 7 | 2 | 15 | 17 | 1 | 25 |
| 8 | 1 | 45 | 18 | 1 | 55 |
| 9 | 3 | 0 | 19 | 2 | 40 |
| 10 | 1 | 15 | 20 | 1 | 55 |

Chart 5. Total residence time in Contactor reactor

Analysis and Conclusions

For the azelaic acid trials, the initial intermediate temperature selected was 150°C based on previous experience. The first trial ramped the temperature to the intermediate target over 60 minutes, then rapidly heating to 204°C over 35 minutes and transferred immediately without a quench to the finishing kettle. This resulted in a reasonable DP of 250°C, bearing in mind that this was not additized and the base oil not optimized. The next trial reduced the intermediate ramp time to 35 minutes, which resulted in a lower DP and lower yield. The third trial replicated the first except for increasing the final ramp time to 60 minutes. This resulted in no change in the DP, although a slight reduction in yield and greater spread between penetrations. The fourth trial replicated the first trial except reducing the intermediate ramp time by approximately 15 minutes; this had negative effects worse than the second trial. The fifth trial allowed a 35 minute intermediate ramp time and 65 minute final ramp time with a comparable overall residence time. This resulted in a marginal increase in DP at close to 260°C with a slight reduction in yield compared to trial 1.

The last three trials included a quench stage in the Contactor reactor. Trial #6 replicated the first trial but included a quench to 182°C over a 25 minute span. This resulted in a DP of over 260°C and a much better yield. The next two trials explored a lower intermediate temperature of 130°C. The seventh batch had a lower intermediate ramp time, but included a hold at the intermediate temperature resulting in holding it at this lower range for 60 minutes, similar to trial #6. However, the final ramp time was slightly longer. This resulted in slight improvements in all test properties. The last trial for azelaic acid reduced the intermediate residence time to 35 minutes, which resulted in a marked negative impact to DP.

The azelaic acid trials showed that a quench in the Contactor reactor yields positive effects for dropping point. These were all one-step procedures, meaning that all the contents were added to the Contactor reactor at the beginning of the reaction stage and then sealed and heated. This is certainly very desirable in simplifying the manufacturing process and minimizing the manufacturing time. Quenching in the Contactor reactor also saves time in finishing. The trials also suggest that allowing approximately 60 minutes in the lower intermediate range produces better dropping points. The study demonstrates that a good dropping point can be achieved with a reaction residence time for azelate complex grease of approximately two hours.

The sebacic acid trials demonstrated a distinctly different reaction profile. In order to achieve a dropping point of 260°C, a two-step procedure was required. The base oil, lithium hydroxide and 12-hydroxystearic acid are placed in the Contactor reactor first, sealed and heated to the intermediate temperature. The contents are then cooled to below 100°C with jacket cooling and the sebacic acid is then added to the Contactor reactor and heated to 204°C. Final quenching in the Contactor reactor had a negative impact on the physical properties of the grease. Batches 14, 15 and 20 had the highest dropping points without the final quenching and were all two-step procedures. As with

the azelaic acid, these trials also demonstrated achieving optimum dropping points with reaction stage residence times of approximately two hours, even with the two-step procedure implemented.

The complexing agent chosen for production could be due to monetary reasons, production reasons or both. Azelaic acid and sebacic acid can both make good lithium complex greases with excellent dropping points (over 260°C) having good yield and mechanical stability as shown by the data. The study clearly demonstrates that these two complexing agents require distinctly different reaction procedures. Further optimization is likely possible with the fully formulated greases to consider the synergistic effects of base oils and additives, which could provide higher dropping points and better yields.

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