Kolates

Aluminum Complex greases are known for their particular advantages of water resistance, good pumpability, high dropping point, and ability to restructure after excursions above their melting points.

This technical bulletin is an introduction to the preparation of these greases using Kolates as the aluminum source, the other raw materials used, the formulation parameters and the necessary equipment.

Materials Needed To Prepare Aluminum Complex Grease

These are the components necessary:

ALUMINUM

BENZOIC ACID

FATTY ACID

OIL

Aluminum

The aluminum will be provided with the Kolate of choice. There are two main Kolates available. The first is the standard cyclic trimer, tri-oxo aluminum tri-isopropoxide, contained in a low viscosity carrier oil. The second is the result of reacting the ring with acids to eliminate the isopropyl alcohol potential during the soap reaction. Both Kolates are in an easily handled liquid form and can be used to prepare industrial or H1 food machinery greases.

Kolate 7013 LV: This is the standard product. It has the aluminum content of 12.7% and is a solution of the cyclic aluminum alkoxide trimer in a low viscosity oil. In appearance it is a clear, nearly colorless, mobile solution and because the oil meets the definition of a technical white oil (CAS 8042-47-5) as established by the FDA and found in CFR 178-3620, this Kolate can be used to prepare H1 food machinery greases.

Kolate 6030: This Kolate has 0.3 mol of benzoic acid and 0.6 mol of fatty acid per mol of aluminum. The aluminum content is 5.3% and is contained in a low viscosity carrier oil. It can be use to prepare food grade H1 greases and does not evolve any alcohol when used to manufacture an aluminum complex grease.

Kolate 7013 LV or Kolate 6030 Variants: It is possible for FedChem to produce variants of either Kolate products to meet a customers special needs. This can entail the substitution of the carrier oil in either product, or a substitution for the type of fatty acid contained in the Kolate 6030.

Kolate Specifications

	Aluminum Content, %	Viscosity, Cps	Minimum Flash Point, °F(°C)	Typical Flash Point, °F(°C)
Kolate 7013 LV	12.7 ± 0.1	80 max	142 (61)	174 (79)
Kolate 6030	5.3 ± 0.1	1400 max	142 (61)	197 (92)

Characteristics Of The Carrier Oil

		Oil for Kolate 7013 LV; 6030
Viscosity SSU	100°F	35
cST	40°C	2.37
Flash Point COC	°F	220
	°C	105
Aniline Point	°F	183
	°C	84
IBP	°F	464
	°C	240
CAS No.		8042-47-5

Benzoic Acid

This can be any technical grade but the flake form is easiest to handle and is generally less dusty.

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Fatty Acid

The fatty acid component is derived from natural sources. Although commonly referred to as stearic, the normal fatty acids used are a mixture of various chain lengths including C-18. Greases are regularly prepared from C-12 acids up to C-20/-22, but by far the most widely used are the various stearic/palmitic blends.

The important characteristics are the acid number, from which the combining weight can be derived, and the Iodine Value, (I.V.), a measure of unsaturation. Both chain length and I.V. have important influences on grease performance. Generally, the best results are obtained with C-16/C-18 acids. A low iodine value is desirable, but acceptable greases can be prepared with higher values and although somewhat softer greases can result, stability is often improved.

Oil

A wide variety of oils can be used to prepare aluminum complex grease, not only straight mineral oils but also synthetic esters and seed oils such as rapeseed and soybean. More often, the base oil is a blend of several mineral oils or blends that include both mineral oils and synthetics.

The two factors to monitor are the viscosity and the aniline point. Viscosities can vary from less than 100 SUS to heavy bright stocks. Generally, high viscosity oils require more soap for a given preparation than do the low viscosity oils. Aniline points are critical in order to prepare the proper mol ratios of the soap constituents. Most greases contain a blend of several kinds of base stocks depending upon the characteristics required, and they may vary widely in aniline point.

It is usually more desirable to make grease in the final blend of the oils but sometimes this may not be possible. Under these circumstances, the soap should be made in the lower viscosity, lower aniline point oil component and the balance of the oil added when the batch has cooled below 125°C. Adding the oils while the batch is still hot can cause a breakdown of the soap and a lower yield than expected. This is particularly true when adding a bright stock.

When the aniline point is higher than 210°F, better yields result if the mol ratio of the benzoic to fatty acid is less than one. The higher the aniline point, the lower this ratio should become in order to get an optimum yield. The relationship between aniline point, the acid ratios, and the yield is illustrated in Figure 1.

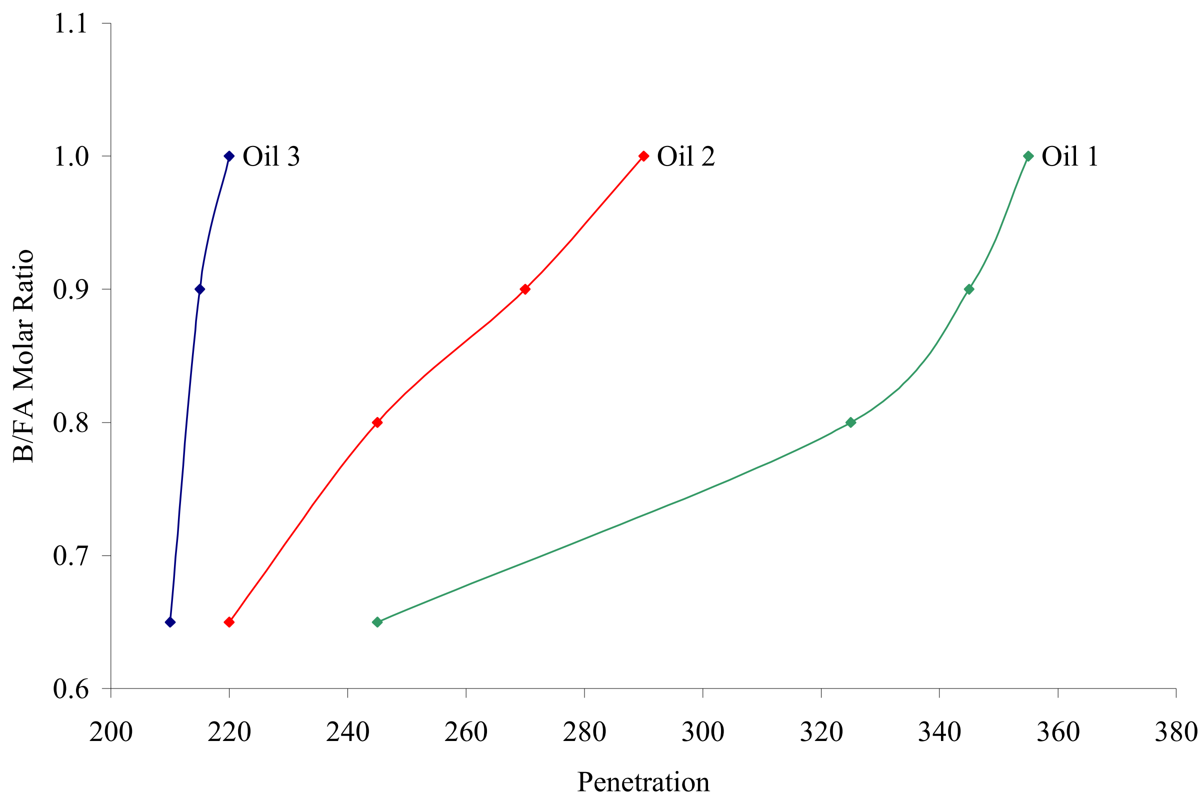

Figure 1

The aniline point of oil 1 is 240°F, oil 2 is 216°F, and oil 3 is 160°F. The viscosities are between 500 and 600 SUS/100°F and the soap content of the three greases plotted is 7.5%. In all cases the mol ratio of the total mols of acid to aluminum is 2:1.

A further refinement in formulation development involves adjusting the ratio of total mols of acids to aluminum in order to optimize the work stability. Oils with aniline points higher than 210°F tend to show a better work stability. It must be remembered that these statements are made in the broadest sense but consideration should always be given to exploring the effect of such adjustments with each oil to be used. In most cases a compromise will be struck which will provide the best over all performance characteristics.

Synthetic base oils such as polyalphaolefins, di-esters, and dimer and polyol esters are easily thickened with the aluminum complex thickener systems. Neat or as mixtures with mineral oil bases, greases made from these fluids provide an additional measure of operational flexibility. In some instances, a higher soap content is necessary but this depends upon the final requirements.

Successful greases can be prepared using rapeseed or sunflower oils usually combined with 10 to 15% medium blown rapeseed oil. The presence of the blown oil allows a more effective soap

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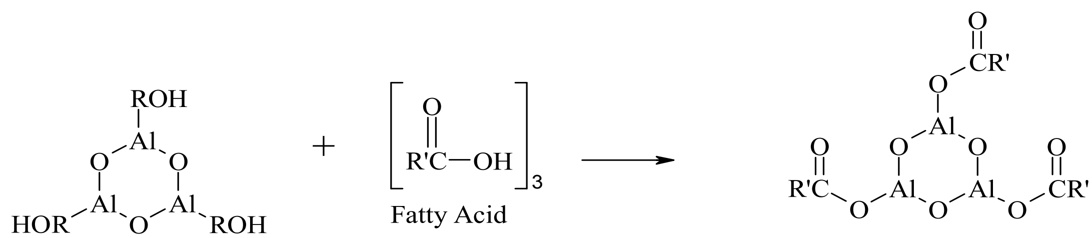
system and thus better yields. They can also be mixed with synthetic esters as well to give broad versatility in formulating.

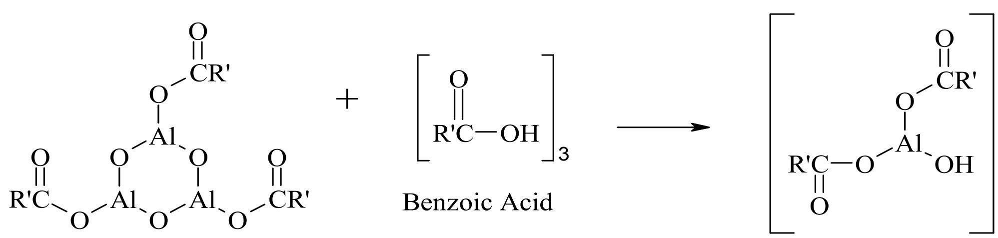
The Kolate Reaction

Standard Kolate is a six-membered ring consisting of alternating aluminum and oxygen atoms. One mol of isopropyl alcohol is attached to each aluminum atom. In theory, in the first step of the reaction, the fatty acid replaces each alcohol on the ring to form a cyclized aluminum monostearate. This takes place at about 100^{o}F. As the temperature increases, the second step begins in which the benzoic acid breaks the ring into three separate molecules of the soap, the aluminum benzoyl, stearoyl hydroxide. This reaction should take place at atmospheric pressure in order to minimize ester formation. With the Kolate 6030, enough of the acid requirement is already in place to eliminate the release of alcohol and it is only necessary to introduce the balance of the acids required for a specific formulation. The general reaction is shown below.

Step One



Step Two



Aluminum Benzoyl Stearoyl
Hydroxide Soap

Typical Formulation

As is shown in Figure 1, more efficient soaps are made with the acids ratios of benzoic to fatty acids of less than one. Assuming the following starting parameters:

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A 650 SUS solvent neutral base stock, with an aniline point of 210°F, a 7.5% soap, with a benzoic to fatty acid mol ratio of 0.75, and a total acids to aluminum mol ratio of 1.9, a typical formulation might be as follows:

5.25% Fatty Acid (F.W. = 272)
1.77% Benzoic Acid
0.48% Aluminum as 100%
92.5% Base Oil
100%

Note that only the 100% aluminum is counted as part of the soap, not the Kolate. In this case, as Kolate LV @ 12.7% aluminum, 3.78% Kolate would be needed and the soap formula would exceed 100%. For practical applications in the grease plant, the whole formulation can be readjusted back to 100%.

There is some latitude in these ratios and for a particular combination of acids the most efficient ratio may require some adjustments. The fatty acid component can be made up of several different acids, each contributing specific characteristics. In such cases the mols of each acid used will be a portion of the total mols of fatty acid required.

To determine the actual weights to be used, it is first necessary to decide on the batch size, and from this, the amount of soap. Using aluminum as the primary constituent, the formulation can be built with the component ratios noted above. If we take as an example, a 1500 pound batch of grease at 7.5% soap content, we will need 112.5 pounds of soap. For every atom of aluminum a total of 1.9 mols of acids will be needed but in a relationship of 0.75 mols of benzoic to 1.0 mol of fatty acid. In this example we will assume a fatty acid with an acid number of 206, giving a combining weight of 272. Using the molecular weights and combining weights of the components, the unit weight relationships are easily determined.

Aluminum		27
Fatty Acid	1.9/1.75 x 1 x 272	295.3
Benzoic Acid	1.9/1.75 x 0.75 x 122	99.3
		421.6

These are now unit weights indicating the proper relationship between the three constituents. The total of 421.6 units as pounds is larger than what is required for the example batch but by multiplying each component by the simple ratio:

112.5/421.6 or 0.2668

This will give the proper amount of each component to use. In this example, the units will be considered in pounds but these numbers can be converted to percent, either of the whole batch or the soap alone.

Staying with pounds, this formula would require:

7.2 pounds of 100% aluminum or 56.7 pounds of Kolate 7013 LV
78.8 pounds of fatty acid
26.5 pounds of benzoic acid
112.5 pounds of soap

Procedure

Add both acids to the kettle containing at least 80% of the total oil to be used and raise the temperature of the solution to between 90°C and 95°C. All the acids should be dissolved and the solution clear. If the temperature goes too high the benzoic acid will begin to sublime. This will quickly be detected by the very irritating odor of the benzoic acid vapors.

At this point the Kolate, previously warmed to room temperature, is added. If the Kolate is too cold, it will result in momentary localized cooling. This may cause some of the benzoic acid to come out of solution in the form of aluminum di-benzoate, an insoluble form of soap which gives the appearance of tapioca. This can not be milled out.

After the Kolate has been introduced, the temperature is allowed to increase to 195°C-200°C where it is held briefly. For lab batches, five minutes is sufficient. For production batches, thirty minutes is enough. This is simply to ensure a complete dispersion of the soap.

Cooling is best accomplished by pumping over to a jacketed cooling kettle. If this is not possible, great care must be used in adding oil to cool the batch because of the danger of breaking the structure. This is particularly true if the cut-back oil is a bright stock. When the temperature reaches 125°C, it is usually safe to put in the additive package and the balance of the oil required.

There are two points to consider in the manufacturing of the grease.

1. It is important that the temperature of the solution be accurately known when the Kolate is added, for if the temperature is much above 95°C, benzoic acid will begin to sublime out of the oil. If allowed to continue, enough can be lost to adversely effect the grease. For this reason, care must be taken to monitor not only the temperature of the kettle contents but also the temperature of the side walls, particularly if the heating is via hot oil. If heated too fast, the temperature of the walls can greatly exceed that of the kettle contents. Benzoic acid losses will occur if agitation is strong enough to splash the contents against the exposed hot wall, even if the contents are still below the sublimation temperature of the acid.
2. When the Kolate is first added, if the heating is stopped, it is possible to leave the batch at this point over night, over the weekend, or longer. This soft gel consistency will not set up. When heating and stirring is resumed it can be finished with no adverse effects. Apparently, once the Kolate is in, the batch is stable indefinitely. This could add some flexibility in production scheduling.

Finishing

Milling equipment is the usual rotor-stator equipment or homogenizer units. In some facilities, milling is done by recirculating back into the cooking vessel. In others, milling into a cooling kettle is practiced. A partially closed or pinched valve in the transfer line will also help to disperse the soap and build yield. With some greases, a light milling just before packaging is all that is needed but much depends on the formulation and the oil used. It is obvious then, that the wide latitude in base oils and fatty acids allows for an equally wide range of process parameters.

Using Kolate 6030

When using Kolate 6030, the steps are exactly the same. The required amount of aluminum is introduced at the same point, just as with Kolate 7013 LV. However, an adjustment must be made in the amount of acids to be added because of the acids included with the Kolate. It may be useful at this point to illustrate the differences in the formula given above for Kolate 7013 LV and the same formula using Kolate 6030 as the aluminum source. The same fatty acid is used in the Kolate 7013 LV example.

	Kolate 7013 LV	Kolate 6030	
FATTY ACID	5.25%	2.32%	…..+ 2.93% from 6030
BENZOIC ACID	1.77%	1.12%	…..+ 0.65% from 6030
ALUMINUM	<u>0.48%</u>	<u>0.48%</u>	
	7.50%	7.50%	
OIL	<u>92.50%</u>	<u>92.50%</u>	
	100.00%	100.00%	

0.48 aluminum requires 3.78 of Kolate 7013 LV and adds 1.98 oil	0.48 aluminum requires 9.06 of Kolate 6030 and adds 4.7 oil
therefore oil to add = 90.3% total batch = 100.0%	therefore oil to add = 87.8% total batch = 100.0%

The small amount of extra oil included with Kolate 7013 LV is usually disregarded and did not appear in the first Kolate formulation. With Kolate 6030, the added amount of oil is now enough to make an adjustment desirable.

Additives

There are a wide variety of additives from which to choose. Most will provide the response required. Generally, oxidation and corrosion inhibitors are needed at from 0.5 to 2.0% while the anti-wear and E.P. components may have to be used at somewhat higher levels depending on the formulation, base oil, and application.

Many end uses will make the addition of a polymer desirable. Again, there are many to choose from. The one offering the best response with aluminum complex greases has been a natural latex at levels of 0.5%. Not only was the yield increased, in most cases the dropping point was not effected.

Food Machinery Greases

One major advantage for the aluminum complex greases is the acceptance of the soap for greases to be used in food machinery applications. These compositions having the possibility of incidental food contact, require an H1 classification by the U.S. Department of Agriculture. The base oil must also comply with CAS # 8042-47-5 which covers technical white oil. For more specific information and typical formulations see the Technical Bulletin on Aluminum complex food machinery greases.

Biodegradable Greases

Aluminum complex greases can be formulated with seed oils and with synthetic esters, as mentioned earlier. Using selected additives, these compositions have good E.P. and anti-wear characteristics as well as satisfactory thermal stability and corrosion resistance. Typical formulations were run in the CEC test, the EPA (Gledhill) test and the modified Strum test. Results were considered acceptable from all three tests, showing high levels of breakdown making them very desirable for use in applications where soil contamination can not be avoided. These would include rail lubricants for both on-board and site lubricators, mining, over road transport, agriculture, and various marine operations.

Further information and help on specific formulations and results are available on request.

Handling and Storage of Kolates

Kolates, as with aluminum alcoholates and reactive acylates, react rapidly and irreversibly with atmospheric moisture to form partial hydrolysis products with consequent loss in expected chemical reactivity. Drum quantities should be stored in dry surroundings, away from the possibility of water collecting on the lids. Laboratory quantities should be kept tightly sealed to maintain reactivity. Partial hydrolysis is evidenced by a skin quickly forming on exposure to moisture in the air. This further develops into a dry crust which may sink to the bottom of the container. If possible, this material should be separated and not used. Only the clear material can be relied upon to provide al the expected reactivity. Hydrolysis of Kolate 7013 LV generates isopropanol. Use suitable safeguards. Personnel should use gloves and eye protection and be provided with adequately ventilated surrounding. Refer to the latest MSDS for complete information on safety and handling.