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"To Bi or not to Bi" – Bismuth in the soap structure

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AXEL
AXEL CHRISTIERNSSON

"To Bi or not to Bi"– Bismuth in the soap structure

Summary

For more than a decade bismuth has been successfully used as an oil soluble EP-additive in lubricating greases.

However, by incorporating bismuth into the soap structure of the grease, instead of having it in the oil phase, the performance of the grease can be further improved. Longer life time, higher operating temperature and improved mechanical stability are some of the advantages you can see.

This paper compares the performance of lubricating grease with bismuth in the soap structure to grease with conventional oil soluble bismuth additives.

Introduction

For a number of years, bismuth naphthenate has been used as an EP additive in greases for steel works and paper mills. One problem has been to get enough EP performance and corrosion protection at the same time as an enhanced high temperature performance. All additives tend to be reactive chemicals and thereby limit the high temperature life of the products. And, if no additives are present, the grease will not perform well anyway. The problem is a sort of Catch 22. Since many years Axel Christiernsson has worked together with Otto Rohr from Miracema-Noudex regarding the use of bismuth as an additive for greases. The first contacts were back in 1992 and since then we have kept in contact.

Basic ideas

The major function of the soap in a grease is to work as thickener. For some soap types, there is also a second effect besides thickening. It can also give EP-performance, corrosion protection or other effects that you normally try to achieve with additives. A typical example of this is calcium sulphonate soap. We have started to call this "functionalised soap". The concept behind this is to move one or more functions normally connected to additives into the soap.

Move the additive from the oil to the soap phase

An old idea of ours has been to move additives from being dissolved in the oil phase to being a part of the soap instead. Since the place for additives to react is at the metal surface, you need to get them there. Normally this happens by using additives which have chemical structures that make them more polar than the soap, so that they can compete against the polar head of soap for access to the metal surface. However, if the additives are too polar, they may also limit the mechanical stability of the finished grease by breaking down the soap. For additives to be useable in a grease, they need to be within this fine area of polarity where they do not break down the soap but are still able to move towards the metal surface and protect it. By moving one or more of the additives to being a part of the soap, the competition for the metal surface gets less.

In this particular case, we move the EP-additive from being dissolved in the oil into being a part of the soap. We incorporate it into a lithium complex soap and thereby counteract the problems of the EP additive changing the mechanical stability of the grease. At the same time, we get a thermally stable soap structure.

Find out what is limiting performance

We need to find out what is limiting the performance and solve the problems with new solutions. To investigate the high temperature performance, one way is to run a thermal stability test on the raw materials to see what the limiting material or materials are. The aim is that one of the main components, such as the soap structure or the base oil, might be identified as the limiting factor for high temperature performance.

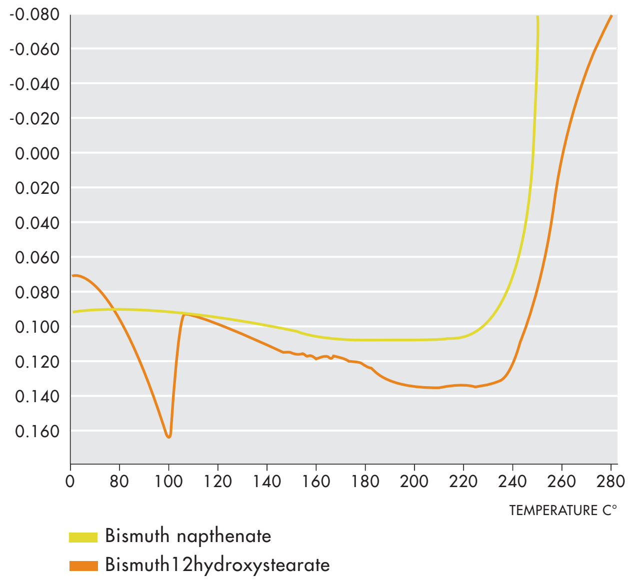
DSC scans were made to investigate this. The tests were run on raw materials as well as finished greases with specific components excluded to see how this would affect the high temperature performance. By doing this, some components could indeed be identified as limiting the performance of the grease. This was evaluated as T-onset temperature to see which material that was most thermally stable. The following table is a comparison of a few different bismuth additives.

DSC SCAN OPEN CUP 5°C / MIN	T-ONSET
BISMUTHOCTOATE	219
BISMUTHNAPHTHENATE	232
BISMUTH12HYDROXYSTEARATE	248

Bismuth naphthenate works well as an EP-additive and also gives some corrosion protection to the grease but, in terms of high temperature performance, this additive is actually one of the limiting components. By making the same type of comparison with possible alternatives such as bismuth octoate, bismuth decanoate and others, it can be seen that, as long as we have the EP-additive dissolved in the oil, we get similar limited high temperature performance, regardless of which type of fatty acid is used. The mechanical stability and EP-performance of the grease will be different depending on which fatty acid the metal is connected to.

If the EP results increase with a certain fatty acid (at the same amount of bismuth metal added to the grease), the mechanical stability of the finished grease may decrease. This is probably dependant on the higher polarity of the additive. If the EP result of the additive decreases, the mechanical stability increases or stays at the same level. One possible way to solve this dilemma is to place the EP-additive in the soap phase.

A DSC SCAN OF PURE BISMUTH-12-HYDROXY-STEARATE



When we look at a DSC scan of pure bismuth-12-hydroxy-stearate, we find a melting point at around 105-110°C and a higher thermal decomposition point compared to the liquid alternative. A lubricating grease with a dropping point of 110°C is however way below what is needed for a high temperature grease.

The solution is to incorporate bismuth-12-hydroxystearate into a lithium complex soap giving a new soap structure (lithium bismuth complex soap). By so doing, we can get a mechanically stable grease with a high dropping point and EP performance built into the soap, (i.e. something we previously called a functionalised soap).

To compare the performance of conventional bismuth additives with the functionalised Bi-Li-soap, we have made a series of greases with a given amount of metallic bismuth with the metal incorporated into the soap structure and comparing this with having a conventional oil soluble additive in the oil phase of the grease. The greases have been evaluated in different standard laboratory tests.

Improved high temperature performance (R2F –B and FAG FE8 tests)

To evaluate the high temperature performance of the grease, we have tested the new formulation in the SKF R2F-B as well as the FE8 test.

The SKF R2F-B is a high temperature functional testing equipment. The test bearing is run at a load of 8500 N and is kept at a given elevated temperature during the test for a period of 20 days. After the test, the grease is studied to see how it has performed regarding oxidation, thickener depletion and its ability to lubricate the bearings. The test result is either a pass or a fail for the specific temperature at which the test has been performed.

SKF R2F-B	BISMUTH AS ADDITIVE IN OIL	BISMUTH AS PART OF THE SOAP
SYNTHETIC BASE OIL LIX 200 CST NLGI 2.5	140°C PASS 150°C BORDERLINE 160°C FAIL	140°C PASS 150°C PASS 160°C PASS
SYNTHETIC BASE OIL LIX 100 CST NLGI 2	140°C PASS 150°C BORDERLINE 160°C FAIL	140°C PASS 150°C PASS 160°C BORDERLINE
MINERAL BASE OIL LIX 700 CST NLGI 1.5	140°C PASS 150°C FAIL 160°C FAIL	140°C PASS 150°C PASS 160°C BORDERLINE

As a second high temperature test, we have also evaluated one specific prototype in the FE8 rig at 160°C and at 30 kN loads.

FE8 AT 160°C 30 KN LOAD	BISMUTH AS ADDITIVE IN OIL	BISMUTH AS PART OF THE SOAP
SYNTHETIC BASE OIL LIX 200 CST NLGI 2.5	FAIL	PASS

Both tests indicate that the new formulations with bismuth incorporated in the soap show improved high temperature performance.

Improved life time in SKF R0F

The SKF R0F test is a lifetime test. Five pairs of bearings run at a specific temperature until breakdown. Running hours are recorded and an average lifetime is calculated. The better lifetime a grease shows, the longer relubrication intervals can be used.

The different test parameters are speed for the bearings between 5.000- 20.000 rpm and temperatures between 120°C and 170°C. The most common speed is 10.000 rpm.

SKF R0F 10.000RPM	BISMUTH AS ADDITIVE IN OIL	BISMUTH AS PART OF THE SOAP
SYNTHETIC BASE OIL LIX 100 CST NLGI 2	L10 150H (120°C) L50 1080H (120°C)	L10 614 (150°C) L50 944 (150°C)

These results mean that the average life time for a bearing at low loads and high speed is about the same for the formulation with bismuth as part of the soap at 150°C as with the old formulation at 120°C. This can also be interpreted as improved lifetime for a specific bearing temperature.

Mechanical stability

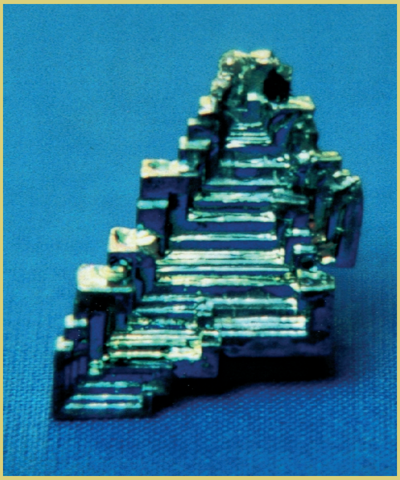
The mechanical stability of the products was evaluated as penetration difference after prolonged working (100.000 ds) as well as in a modified Shell Roll Stability test. The modified Shell Roll Stability is much more severe compared to the standard test and runs at 80°C for 50 hours instead of 2 hours at room temperature.

SHELL ROLL STABILITY 50H/80°C	BISMUTH AS ADDITIVE IN OIL	BISMUTH AS PART OF THE SOAP	IMPROVEMENT UNITS
SYNTHETIC BASE OIL LIX 200 CST NLGI 2.5	+50	+30	20
SYNTHETIC BASE OIL LIX 150 CST NLGI 1.5	+45	+27	18
SYNTHETIC BASE OIL LIX 100 CST NLGI 2	+35	+15	20
SYNTHETIC BASE OIL LIX 450 CST NLGI 2	+40	+27	13
MINERAL BASE OIL LIX 700 CST NLGI 1.5	+50	+36	14

In the results from the Shell Roll Stability we can see an improved mechanical stability of the grease with varying NLGI grades, base oil types and base oil viscosities.

PROLONGED WORK PEN DIFF 100.000	BISMUTH AS ADDITIVE IN OIL	BISMUTH AS PART OF THE SOAP	IMPROVEMENT UNITS
SYNTHETIC BASE OIL LIX 200 CST NLGI 2.5	+28	+20	8
SYNTHETIC BASE OIL LIX 150 CST NLGI 1.5	+19	+10	9
SYNTHETIC BASE OIL LIX 100 CST NLGI 2	+22	+19	3
MINERAL BASE OIL LIX 700 CST NLGI 1.5	+31	+20	11

The same thing can be seen in the prolonged penetration results. Both those tests indicate that we achieve an improved mechanical stability by having bismuth incorporated into the soap compared to conventional bismuth carboxylate.



THE MAYAN GREAT JAGUAR TEMPLE RESEMBLES A BISMUTH CRYSTAL

Otherwise retained performance levels. Low temp, EP etc

When you make major changes in the formulation, like changing the soap structure, you must also be careful not to negatively influence other parameters. We have therefore also looked into how the changes will affect other properties.

START AND RUNNING TORQUE - 40°C	BISMUTH AS ADDITIVE IN OIL	BISMUTH AS PART OF THE SOAP
SYNTHETIC BASE OIL LIX 100 CST NLGI 2	START 0.59NM RUNNING 0.06 NM	START 0.60 NM RUNNING 0.06 NM
SYNTHETIC BASE OIL LIX 200 CST NLGI 2.5	START 0.52 NM RUNNING 0.12 NM	START 0.90NM RUNNING 0.11 NM

PROPERTY MEASURED	BISMUTH AS ADDITIVE IN OIL SYNTHETIC BASE OIL LIX 200 CST NLGI 2	BISMUTH AS PART OF THE SOAP SYNTHETIC BASE OIL LIX 200 CST NLGI 2
EMCOR WWO DIST WATER	0-0	0-0
EMCOR WWO SALT WATER	2-3	2-3
DROPPING POINT	>280°C	>280°C
COPPER CORROSION 100°C / 24H	1B	1B
OIL BLEEDING 168H/40°C	1.5%	1.6%
4BALL WELD LOAD	3600 N	3800 N
4BALL WEAR SCAR 400N 1H	0.68 MM	0.70 MM

Summary and conclusions

By moving the bismuth additive from the oil to being a part of the soap, we can see the following advantages without finding any disadvantages in other properties:

Improved high temperature performance or life-time: A grease with bismuth incorporated into the soap can run constantly at higher temperatures compared to a grease containing conventional bismuth carboxylate. This is probably due to the thermal decomposition of the conventional bismuth additives.

Improved mechanical stability:
By looking at the result of the soap structure tests, it can be seen that the mechanical stability is improved. There are probably two reasons for this. Higher soap content often helps the grease to be more mechanical stable. Most bismuth carboxylates limit the stability of the soap as they are fairly polar substances.

References:
O Rohr, R. Hissa – "Preformed soap as thickener and EP-additive for grease production." (2004)

O. Rohr – "Bismuth - The new ecologically green metal for modern lubricating engineering." (2002)

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