ELSEVIER

Thermochimica Acta 282/283 (1996) 493–499

thermochimica
acta

Characterization of lubricants used in the metalworking industry by thermoanalytical methods[1]

Bengt O. Haglund[a,*], Per Enghag[b]

[a] *AB Sandvik Coromant, S-126 80 Stockholm, Sweden*
[b] *Materialteknik HB, Stortorget 17, S-702 11 Örebro, Sweden*

Abstract

In the cold-rolling of steel strip as well as the cold-drawing of steel wire, different mixtures of organic and inorganic compounds are used to lower the friction. Such lubricants may age or deteriorate during use. It has been shown that a thermoanalytical method involving oxidation in pure oxygen can be used to characterize the changed properties in such lubricants. The method can also be used to distinguish different kinds of lubricants.

Keywords: Cold rolling; Wire drawing; Lubricant; Oil; Thermogravimetry; TG; Differential thermal analysis; DTA

---

1. Types of lubricants

In the cold-rolling of strip steel, the rolling mills must be lubricated and cooled by applying an oil or an oil–water emulsion. Emulsions are often used due to their better cooling capacities compared to pure oils. For economical and environmental reasons, the emulsion is recirculated and can be used for several months. The composition of emulsions is often very complex, containing, for example, concentrated oils, fats, tensides, emulgators, antioxidants, esters, corrosion inhibitors and antifoaming agents.

In wire-drawing,the lubricants used can be oils or emulsions (wet-drawing) or solid lubricants such as sodium or calcium stearate (dry-drawing).

In the case of dry-drawing, one also uses lubricants carriers, e.g. zinc phosphate, borax, lime, etc., together with the lubricants. At the high temperatures created by deformation and friction heat, the lubricants will melt, but the carriers will not. The

---

* Corresponding author.

[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

0040-6031/96/$15.00 © 1996 – Elsevier Science B.V. All rights reserved
SSDI 0040-6031(96)02825-0

lubricant system in the drawing die will thus be a mixture of solid carrier particles in a molten soap.

2. Deterioration mechanisms

On rolling and drawing in emulsions, fats are attacked by water and converted to fatty acids and alcohols. The pH value of the emulsion is lowered mainly due to overdraw of acids from the cleaning, rinsing and, possibly also, plating processes before the rolling and drawing step. Neutralization is detrimental as it increases the salt content and the risk for the emulsion break down.

On dry-drawing, the lubricant molecules can be broken down due to oxidation. The first step in this oxidation is peroxide formation which starts preferentially at a double bond in the molecule. When the molecules are broken, the lubrication fails, welded junctions are created, adhesive wear occurs and the wire surface is damaged. With this in mind, it is easy to see that thermoanalytical methods are a valuable way to characterize different lubricants and lubricant mixtures.

To summarize, it can be stated that solid or liquid lubricants and emulsions may break down by one or more of the following mechanisms:

(i) Oxidation. Double bonds in the fat are attacked by oxygen. Fatty acids, alcohols or aldehydes are formed.
(ii) Hydrolysis. The fats are attacked by water and converted to fatty acids and alcohols. The pH value of the emulsion is lowered.
(iii) Thermal degradation. Polymerization due to the high pressure and temperature during passage between the rolls or in the drawing die. Formation of new compounds or solutions between components in the original lubricants may occur, leading to changed properties.
(iv) Evaporation. Volatile components disappear due to the high temperature.

3. Analytical methods

Several analytical methods are used to characterize new or used lubricants [1]. Due to the complex compositon of the lubricants, different methods are often used at the same time, as there is no single method to characterize all aspects of the condition of the lubricant. For the characterization of lubricants, conventional physical and chemical analytical techniques are used, but also modern physical methods, mainly infrared spectroscopy (IR) and gas chromatography (GC). During recent years, oxidation resistance as determined by thermoanalytical methods has been used more [2–8] and national and international standards have been established [9]. The importance of such methods is the possibility to obtain conditions, which are close to the real conditions when the lubricants are used. It is, however, almost impossible to simulate the conditions exactly.

A combination of two or more thermoanalytical methods has been found to be very efficient to characterize the properties of a lubricant. The basic methods are differential thermal analysis (DTA) or differential scanning calorimetry (DSC) by which the onset of reactions can be determined as well as the nature and the heat of reactions. Besides this, thermogravimetry (TG) gives information about weight losses due to evaporation or formation of volatile compounds. The time derivatives of these measured values are important for the study of the reaction rates. A combination with mass spectrometry or gas chromatography may give further information about the reactions.

The atmosphere used in the thermoanalytical measurements is generally pure oxygen at ambient [3, 5–8] or increased pressure [4]. Air at increased pressure was previously used [2]. Normally this is not a true simulation of the real conditions but reactions are enhanced and peaks become more evident under these conditions.

4. Applications and results

Two applications will be described: liquid lubricants used in cold-rolling and solid lubricants used in wire-drawing.

Emulsions cannot be analysed directly, but have to be separated by ether extraction into an oil phase and a water phase [1]. The thermal analysis of the oil phase is made at a constant heating rate, normally 5 K min^{-1}. An example of the results is given in Ref. [10], from which Fig. 1 is reproduced. It has been found that the oxidation onset temperature is about 165°C for a fresh emulsion oil phase. The oxidation onset temperature is gradually increased to over 200°C when the same emulsion has been used for about half a year. The reproducibility of the test is good and the range of three subsequent determinations is less than 3–4°C.

The use of a simultaneous TG–DSC technique is beneficial as the TG recording shows the amount of volatile components in the emulsion. It is also valuable for the establishment of the DSC baseline. The first significant deviation from the TG baseline is often easily detected and coincides generally with the onset of the DSC peak.

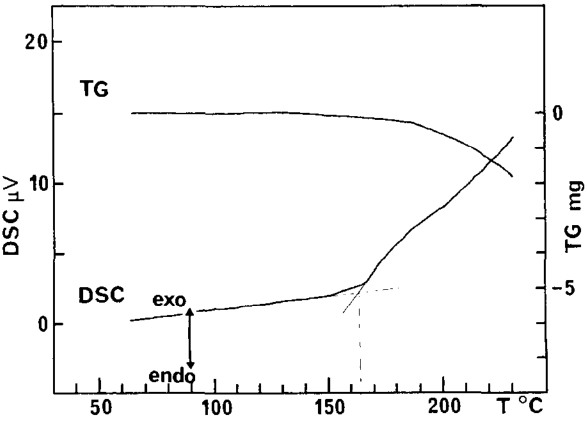

Fig. 1. Oxidation stability of the oil phase of an unused oil–water emulsion for cold-rolling of steel.

Another application of the simultaneous TG–DSC technique is the determination of the solubility of polyethylene glycols with different molecular weights in water–ethanol solutions of different concentrations and temperatures [13].

Solid lubricants for wire-drawing often show more details both in the DSC and TG curves. It is also valuable to analyse the lubricant residue which has passed the drawing die and compare the results with those from the unused lubricant.

From earlier investigations [11], different lubricants have been classified in four types:

(i) Type A (Fig. 2). The lubricant is easily oxidized in the drawing die. The residue behind the die has already become strongly oxidized and is thus a more resistant "slag

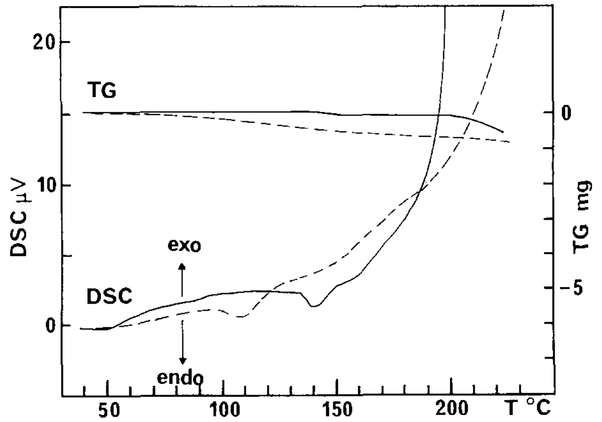

Fig. 2. DSC and TG recordings from a dry-drawing lubricant of sodium type. Type A: full line, lubricant; and dashed line, residue.

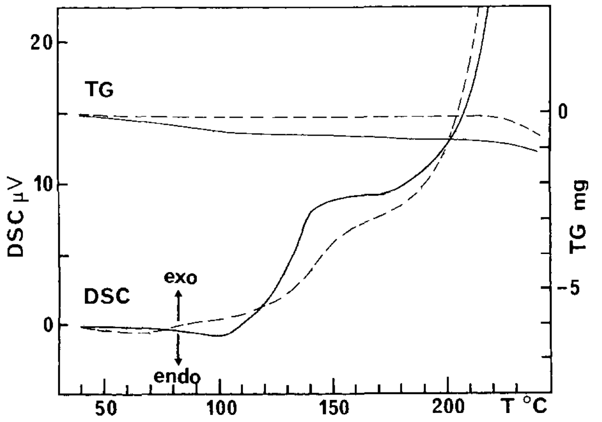

Fig. 3. DSC and TG recordings from a dry-drawing lubricant of sodium type. Type B: full line, lubricant; and dashed line, residue.

product" in the subsequent thermoanalytical test. The DSC curve is typical for a sodium lubricant with some content of unsaturated fatty acids.

(ii) Type B (Fig. 3). Endothermic melting reactions occur on heating. The melt protects the lubricant from oxidation in the die. The DSC curve shows a marked plateau. This is typical for a calcium stearate lubricant. The oxidation curves for the lubricant and for the residue are rather similar. (Note that the designations sodium and calcium stearate are not quite correct. The acids of the soaps are mixtures of different fatty acids, although sodium or calcium stearate is the main component.)

(iii) Type C (Fig. 4). The lubricant is very stable and is not oxidized during the drawing operation. No endothermic processes occur. The residue behaves similarly to the lubricant. The onset temperature for the oxidation is high both for the lubricant and for the residue.

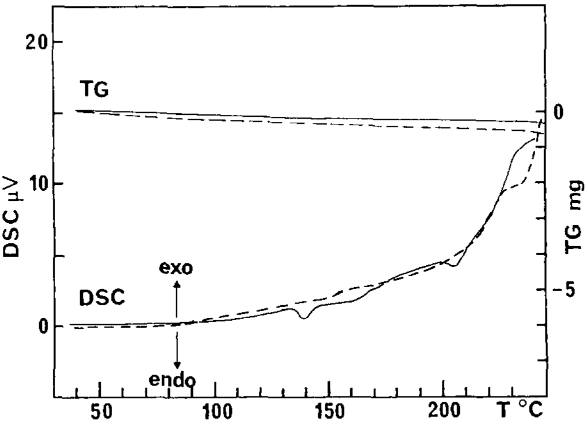

Fig. 4. DSC and TG recordings from a very stable and oxidation-resistant dry-drawing lubricant. Type C: full line, lubricant; and dashed line, residue.

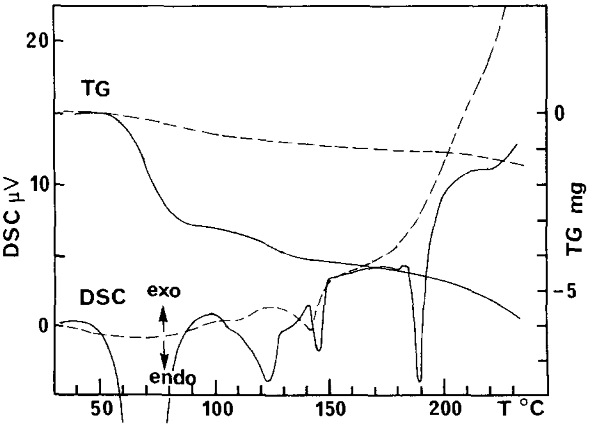

Fig. 5. DSC and TG recordings from a synthetic dry-drawing lubricant. Type D: full line, lubricant; and dashed line, residue.

(iv) Type D (Fig. 5). Strong endothermic processes (both melting and evaporation) occur in the die and keep the working temperature of the lubricant relatively low. The corresponding cooling effect also keeps the oxidation at a low rate. This is typical for synthetic lubricants.

In the residue, these reactions do not repeat as they are mainly irreversible. Thus the oxidation of the residue occurs at a lower temperature than that of the unused lubricant.

As an application example, a comparison between two dry-drawing lubricants will be mentioned. From practice, it was found that they had different behaviours in the drawing operation, one better than the other. A thermoanalytical investigation was

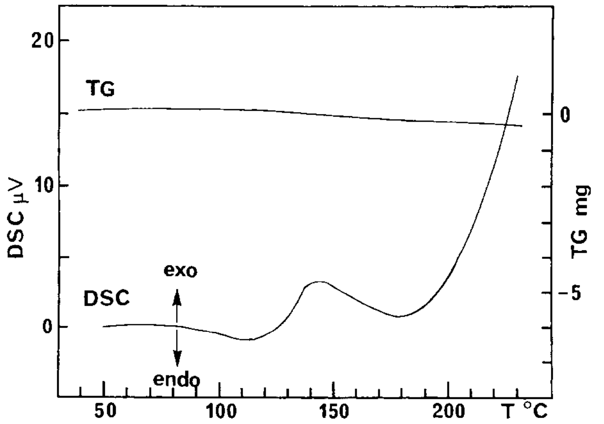

Fig. 6. DSC and TG curves from a test sample of a dry-drawing lubricant with good drawing properties (sample I). Loss of mass from water evaporation, 0.37%.

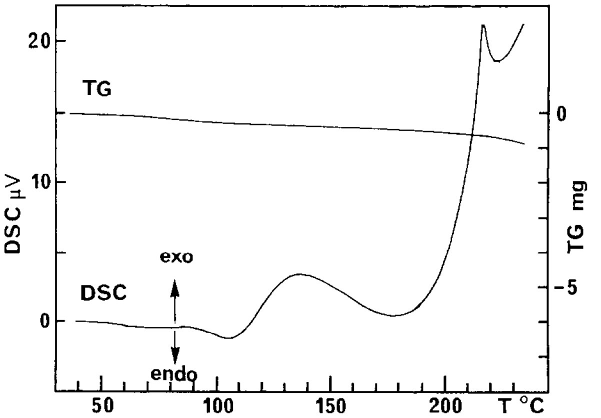

Fig. 7. DSC and TG curves from a test sample of a dry-drawing lubricant with good drawing properties (sample II). Loss of mass from water evaporation, 1.12%.

made using the above-mentioned simultaneous technique. The results are shown in Figs. 6 and 7 for samples **I** and **II**, respectively.

According to the experimental results, the two lubricants are very similar. Both show the plateau at about 150 °C which is typical for a calcium soap. For sample **II** there is, however, also an indication of melting (endothermic reaction) at about 200 °C **within** the exothermic region. Thus some sodium stearate seems to be present in sample **II**.

The important difference between the two lubricants is, however, not in the chemical composition. From the TG and DSC curves in the region 60–110 °C, in which the water evaporation takes place, one can calculate that the water content of sample **II** is three times higher than that of sample **I** and it is well-known that water is detrimental for dry-drawing operations. Lubricant **I** thus ought to have better lubricating properties. This was also what was found in practice.

5. Summary

Simultaneous DSC–TG or DTA–TG thermal analysis has been used for the characterization of solid or liquid lubricants in the metalworking industry. The impact of the technique is clearly demonstrated by its possibilities in distinguishing between different types of reactions such as evaporation, melting and oxidation.

References

[1] D. Svedung, The analytical control of cold rolling emulsions, Scand. J. Metall., 5 (1980) 183–187.

[2] F. Noel, The characterization of lube oils by DSC analysis, J. Inst. Petrol., 57 (1971) 354.

[3] C. Lovász, Thermische Stabilität von Schmierstoffen, Erdöl und Kohle–Erdgas, 30 (1977) 219–223.

[4] J.A. Walker and W. Tsang, Characterization of lubricating oils by differential scanning calorimetry, SAE Technical Report Series 801383 (1980) Oct.

[5] A.K. Biswas et al., Evaluation of antioxidants in lubrication oils by differential thermal analysis and IR spectroscopy, Wear 82 (1982) 45–48.

[6] H. Kopsch, and E. Wedepohl, Zur Prüfung Schmierölen mit thermoanalytischen Methoden, Tribologi + Schmierungstechnik, 30 (1983) 132–138.

[7] S.H. Goh, Thermoanalytical studies of rubber oxidation: Prediction of isothermal induction time, Thermochim. Acta, 75 (1984) 323–328.

[8] R. Riesen, Oxidationsstabilität von Speise-Ölen und -Fetten, Mettler Application TA3000 Nr. 3001.

[9] Plaströr–Termoanalytiska metoder för bestämning av oxidationsstabilitet, Svensk Standard SS 3579 Utg. 1987-09-15. (Plastics pipes–Thermoanalytical test methods for the determination of oxidation stability).

[10] B.O. Haglund, and T. Luks, Characterisation of the ageing of cold rolling emulsions by differential scanning calorimetry, Thermochim. Acta, 72 (1984) 51–54.

[11] T. Luks, B.O. Haglund and P. Enghag, Characterization of drawing lubricants by thermal analysis, Thermochim. Acta, 95 (1985) 413–418.

[12] P. Enghag, B.O. Haglund and T. Luks, Investigation of dry drawing lubricants by differential scanning calorimetry, Wire Journal International, May (1986) 48–53.

[13] B.O. Haglund and R. Svensson, A thermoanalytic method for the study of the solubility of polyethylene glycols in ethanol and water, J. Therm. Anal., 35 (1989) 391–395.