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CHARACTERIZATION OF SILVER FLAKE LUBRICANTS

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Abstract

There is a thin layer of organic lubricant on commercial silver (Ag) flakes that are widely used as the fillers in electrically conductive adhesives (ECAs). This lubricant layer highly affects the properties such as conductivity of the ECAs. Therefore, understanding the behavior of Ag flake lubricant layer is essential for developing high performance ECAs. This work is aimed at studying the chemical nature of the lubricant layer, interaction between the lubricant layer and Ag flakes, and thermal behavior of the lubricants during heating. A blank Ag powder is ball-milled into Ag flakes with five fatty acids that have different carbon–hydrogen chain length as lubricants. After lubrication, the Ag flakes are studied using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and thermogravimetry (TG), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). It is found that (i) Ag flakes lubricated with fatty acids of different chain lengths have exothermic DSC peaks and mass losses at different temperatures, (ii) the lubricant layer on the lubricated Ag flake surfaces is a salt formed between the acid and Ag, and (iii) exothermic DSC peaks (in air) of a lubricated Ag flake is probably due to the oxidation of lubricant layer on the Ag flake surface.

Keywords: characterization, fatty acids, interaction, lubricants, silver flakes, thermal behavior

Introduction

The continued evolution of electronics industry has created a need for user-friendly alternatives to traditional lead-bearing solders. Eliminating toxic lead and harmful solvents during flux cleaning are the primary environmental concerns favoring electrically conductive adhesives (ECAs). The pressure to reduce the industrial use of lead is growing, particularly in Europe. Legislation has already been proposed to eliminate lead-containing solders [1]. ECAs are an environmentally friendly alternative to solders. Compared to solders, ECAs have lots of advantages such as low temperature processing, low thermomechanical fatigue, non-toxic, finer pitch capability [2–9].

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ECAs are composites of non-conductive polymeric resin matrix and highly conductive metallic fillers. Among all of the metallic fillers, silver (Ag) flakes are most widely used in formulating ECAs because Ag and silver oxide both have very high electrical conductivity.

Commercial Ag flakes generally are produced from Ag powders by a ball-milling process. In order to prevent cold welding of the silver particles, it is necessary to use an organic lubricant, generally a fatty acid, during the ball-milling [10]. A thin layer of the lubricant remains on the Ag flake surface after the production processing. This layer of lubricant highly affects ECA properties including viscosity of the conductive adhesive and conductivity of the ECA after cure [11]. Even though Ag flakes have been employed in conductive adhesives for a long time, fundamental understanding of silver flake lubricant layer lags far behind the practical applications of the Ag flakes. Fully understanding of Ag flake lubricants is essential in order to develop high performance ECAs. In this paper, chemical nature of Ag flake lubricant layer, interaction between lubricant layer and Ag flakes, and thermal behavior of the lubricants were investigated.

Experimental

Materials

A blank Ag powder was bought from Chemet Company. Fatty acids including decanoic acid, lauric acid, myristic acid, palmitic acid, and stearic acid were purchased from Aldrich Chemical Company. Chemical structures and some physical properties of these fatty acids are given in Table 1. Anhydrous ethanol and stainless balls (4 mm diameter) were also obtained from Aldrich Chemical Company. Ag stearate (95% purity) was supplied by Bodman Industries Incorporated. All of the chemicals were used as received.

Lubrication of a blank Ag powder

A blank Ag powder was lubricated with five different fatty acids by a ball-milling process. Lubrication was based on the following procedure: (1) dissolve 2.0 g of each acid in 10 ml ethanol in a 50 ml bottle, (2) add 5.0 g of the blank Ag powder and some stainless balls in the solution, (3) put the bottles on a ball-milling machine, (4) after one week ball-milling, the Ag particles were removed from the bottles and washed with ethanol five times, (5) dry the Ag powders at room temperature under a vacuum. The Ag powders lubricated with acid 10, acid 12, acid 14, acid 16, and acid 18 were called Ag (10), Ag (12), Ag (14), Ag (16), and Ag (18), respectively, in later sections.

Study of Ag powder morphology

The morphology change of Ag powders during lubrication was investigated using a scanning electron microscope (SEM) from Hitachi, model S-800. A small amount of

Table 1 Chemical structures and properties of some fatty acids

Acid IUPAC name (trival name)	Chemical structure	Melting temperature/°C	Purity/%	Names called in the later sections	Boiling point T_b/°C [12]
Decanoic acid (capric acid)	$CH_3(CH_2)_8COOH$	31–32	99	acid 10	270
Dodecanoic acid (lauric acid)	$CH_3(CH_2)_{10}COOH$	44–46	99.5	acid 12	225 (at 100 mm Hg)
Tetradecanoic acid (myristic acid)	$CH_3(CH_2)_{12}COOH$	54–55	99	acid 14	250 (at 100 mm Hg)
Hexadecanoic acid (palmitic acid)	$CH_3(CH_2)_{14}COOH$	61–64	99	acid 16	350
Octadecanoic acid (stearic acid)	$CH_3(CH_2)_{16}COOH$	67–69	99	acid 18	360

an Ag powder was placed on an aluminum SEM sample holder. After gold sputtering, the sample was studied using the SEM.

Study of lubricants and lubricated Ag particles using DSC

A differential scanning calorimeter (DSC) from TA Instruments, model 2970, was used to study the fatty acid lubricants and the lubricated Ag particles. A sample of approximately 10 mg was placed in an aluminum DSC open pan. After the sample was put in the DSC cell, the temperature was raised from 25 to 350°C at a heating rate of 10°C min^{-1} either in an air or a nitrogen purge gas and heat flow was recorded.

Study of lubricants and lubricated Ag particles using TG

The fatty acid lubricants and the lubricated Ag particles were studied using thermogravimetry (TG) from TA Instruments, model 2950. A sample of about 30 mg was placed in a platinum TG pan. The sample was heated from 25 to 350°C at a heating rate of 10°C min^{-1} in either an air or a nitrogen purge gas. Mass loss of the sample during heating was recorded.

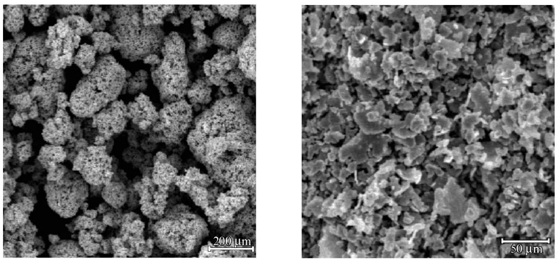
Study of lubricated Ag particles using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS spectra of the lubricated Ag flakes were collected using a Fourier Transform Infrared Spectrometer with a DRIFTS accessory from Nicolet, model Magna 560. Sample preparation and data collection procedure for DRIFTS study were as follows: (a) mix 100 mg of an Ag flake with 0.5 g of IR grade potassium bromide (KBr), (b) place the mixture in a DRIFTS pan, and (c) collect a spectrum.

Results and discussion

Lubrication of a blank Ag powder

Our previous study showed that (1) a commercial Ag flake showed an exothermic DSC peak and (2) commercial Ag flakes from different manufacturers tended to have



Before lubrication After lubrication

Fig. 1 Morphology change of an Ag powder during lubrication exothermic peaks at different temperatures [11]. However, exact chemical structures of the lubricants on those Ag flakes were not known. In this study, a blank silver powder was lubricated with five fatty acids which had similar chemical structures but different carbon hydrogen chain length. Based on SEM study results, it was found that, after lubrication, morphology of the Ag powders changed from spherical powders to flakes. All of the lubricated Ag powders had similar morphology. The SEM photos of the blank Ag powder and one of the lubricated powders, Ag (18), are shown in Fig. 1.

Thermal study of lubricants

Fatty acids used in the lubrication were studied using a DSC in an air and a nitrogen purge gas and results are shown in Figs 2(a) and 2(b), respectively. All of the fatty acids showed a sharp endothermic peak at a low temperature range (less than 100°C) that is the melting temperature of each acid. The melting temperatures, which are the peak temperatures of the melting peak of the DSC curves, of the fatty acids are given in Table 1. The curves below 100C are not displayed in Fig. 2. For each acid, there is an endothermic peak at a lower temperature followed by an exothermic peak at a higher temperature when the purge gas is air. However, in nitrogen, each of the acids only showed one endothermic peak which appeared at about the same temperature

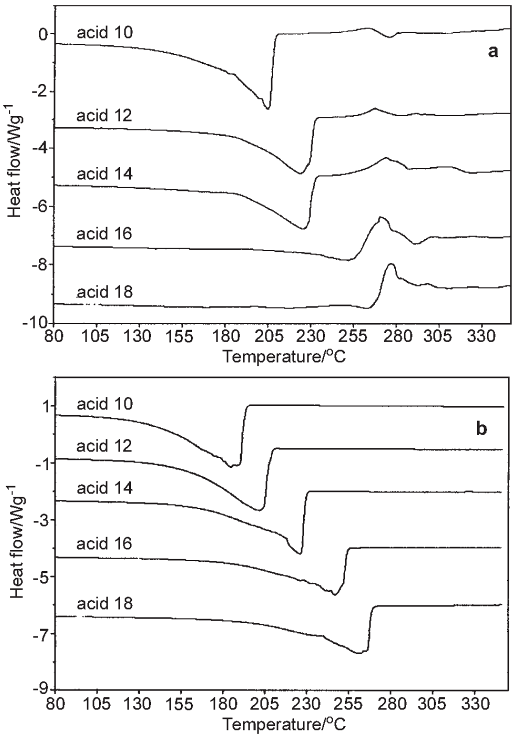


Fig. 2 DSC dynamic scans of five fatty acids in air (a) and nitrogen (b)

range as the endothermic peak in air. Also, no residue was found in the DSC pan after the run in nitrogen. The fact that a fatty acid showed an endothermic peak in both air and nitrogen atmospheres indicated that the endothermic probably corresponds to vaporization (degradation) of the acid. Absence of the exothermic peak in nitrogen suggests that the exothermic peak in air is due to the oxidation of acid left in the DSC pan after vaporization. The endothermic peak shifted to a higher temperature in air and nitrogen for the fatty acid with a longer carbon hydrogen chain. This is because a fatty acid with a long chain has a higher vaporization (degradation) temperature. In addition, with increasing chain length, an acid showed a smaller endothermic peak and a larger exothermic peak. This is probably due to the slower vaporization process of an acid with a longer chain. Therefore, more of the acid remains in the pan and thus more heat is generated after the residual acid is oxidized.

Mass loss during heating of these fatty acids was investigated using TG in an air and a nitrogen purge gas and results are given in Figs 3(a) and 3(b), respectively. All of the acids showed similar mass loss trends. For a fatty acid, no appreciable mass loss difference could be observed in air and in nitrogen. However, acids with a longer chain showed a significant mass loss in a higher temperature range. As compared with Fig. 2, it was observed that, for an acid, significant mass loss happened at the same temperature as endothermic peak in its DSC curve. This suggested that the mass loss of a fatty acid was probably due to a vaporization (degradation) of the acid.

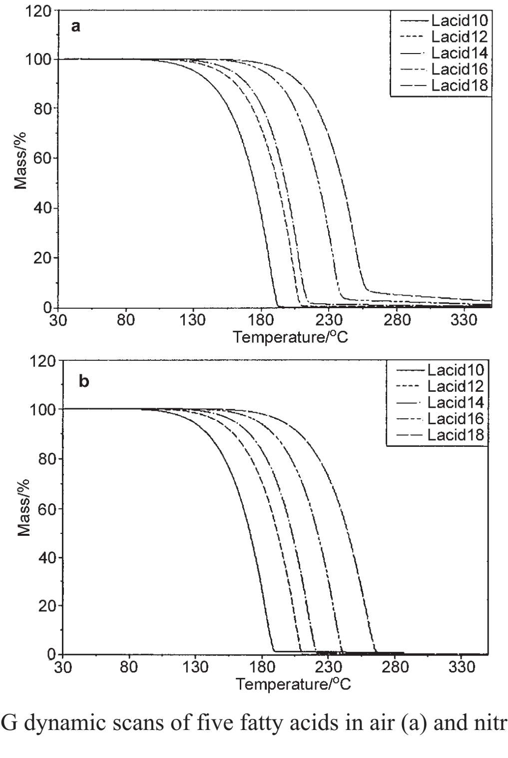


Fig. 3 TG dynamic scans of five fatty acids in air (a) and nitrogen (b)

Thermal study of the lubricated Ag particles

The blank Ag powder and the Ag flakes lubricated with different fatty acids were studied using a DSC in an air purge gas and results are given in Fig. 4. As can be seen from the Figure, all of the Ag flakes showed two adjacent exothermic DSC peaks, one of which is broad and the other is sharp (at higher temperatures). But the blank Ag powder did not have any DSC peak. Therefore some fatty acid must have remained on the Ag flake surfaces after the lubrication process. However, in the DSC curves of these Ag flakes, there were no endothermic peaks at the temperature range of melting point of each fatty acid. This indicated the lubricant of the Ag flake surface was not in the form of free acid or no longer crystalline. In addition, compared to DSC curves in Fig. 2, the exothermic peaks of each Ag flake were different from that of its corre-

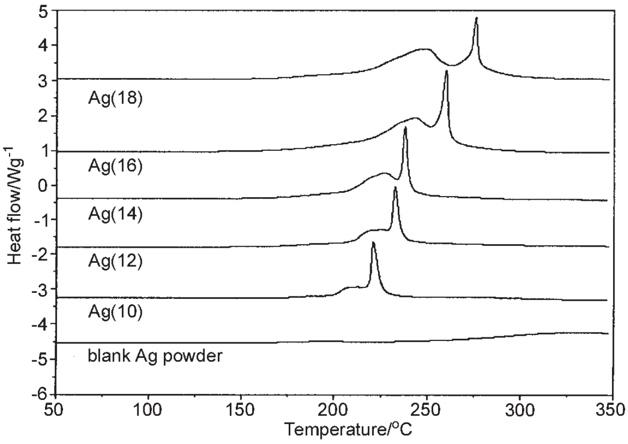


Fig. 4 DSC dynamic scans (in air) of a blank Ag powder and Ag flakes lubricated with five fatty acids

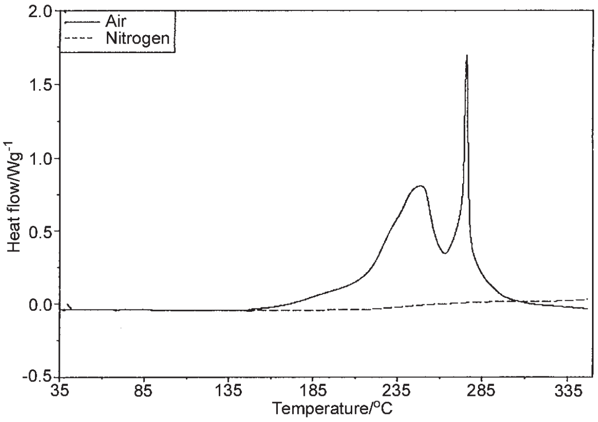


Fig. 5 DSC dynamic scans of Ag (18) in N_2 and air

sponding fatty acid. These results suggested there must be some interaction between the fatty acid and Ag flake. In addition, Ag flakes lubricated with a fatty acid of longer carbon hydrogen chain showed the exothermic peaks at higher temperatures.

These Ag flakes were also studied by DSC dynamic scan under a nitrogen (N_2) atmosphere. All of them showed the same results: no exothermic peaks. Only the results of the Ag flake, Ag (18), lubricated with stearic acid (acid 18) are shown in Fig. 5 and compared. Absence of the exothermic DSC peak in nitrogen suggested that the exothermic DSC peaks in air were probably due to oxidation of the organic lubricant on the Ag flake.

Mass losses of these lubricated Ag flakes and the blank Ag powder were studied using TG in an air purge gas and mass loss *vs.* temperature is shown in Fig. 6. All of the Ag flakes showed much more significant mass losses than the blank Ag powder. This again indicated that some of the lubricant stays on the Ag flake surface after lubrication. The mass loss onset temperature of the Ag flake lubri-

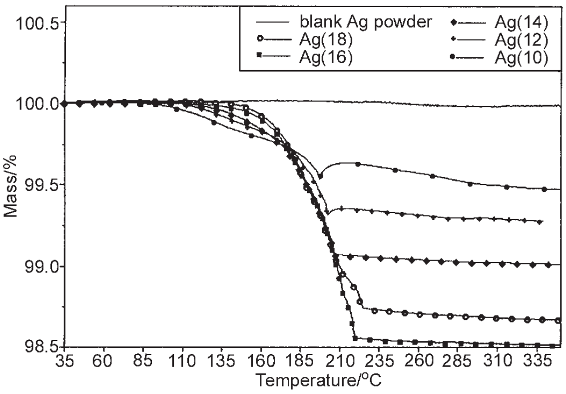


Fig. 6 TG dynamic scans of five lubricated Ag flakes and a blank Ag powder

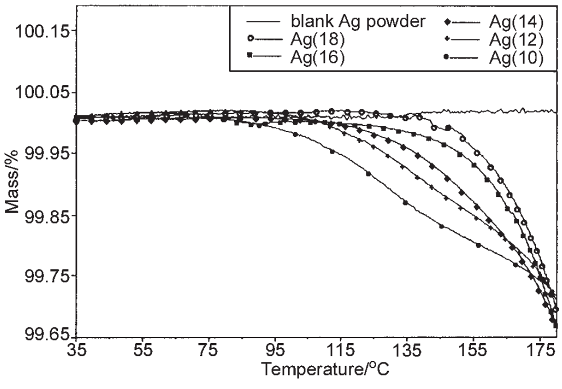


Fig. 7 Onsets of TG curves of five lubricated Ag flakes and a blank Ag powder

cated with a longer acid was higher (Fig. 7). As compared with the TG curves in Fig. 3, mass loss curve of each lubricated Ag flake was different from that of its corresponding fatty acid. Therefore, there may be some kind of interaction between the lubricant layer and the Ag flake, e.g. formation of Ag stearate.

Study of interaction between lubricant layer and Ag flakes

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) study of lubricated Ag flakes

Diffuse reflectance infrared is a powerful technique to characterize the chemical nature of organic substances on powder surfaces. All of the lubricated Ag flakes and the original blank Ag powder were studied using DRIFTS. All of the lubricated Ag flakes showed similar DRIFTS spectra, therefore, only one of the Ag flakes, Ag (18), was presented here. For comparison, the DRIFTS spectra of the blank Ag powder and acid 18, stearic acid, were also collected under the same condition. The spectra of these materials are shown in Fig. 8. Assignments of peaks of the spectra are given in Table 2. The absence of a strong band near 1700 cm^{-1}, which corresponds to the C=O stretching of –COOH group, in the spectrum of Ag (18) indicates that the lubricant layer on Ag (18) was not free stearic acid. The presence of two new near bands at 1560 and 1410 cm^{-1}, which correspond to the asymmetric and symmetric stretching of carboxylate group –COO^{-} respectively [13–15] in the spectrum of Ag (18) suggests that the chemistry between the carboxylic acid head-group and the Ag surface yields a full conversion of the acid to a carboxylate salt, Ag stearate.

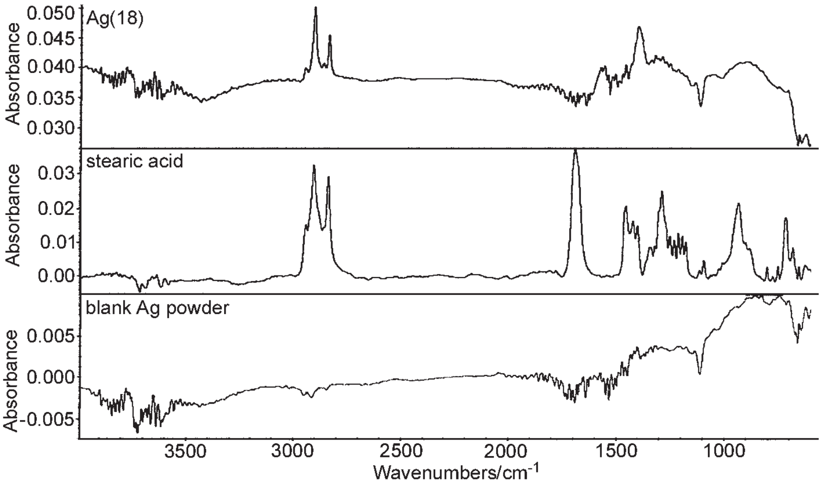


Fig. 8 DRIFTS spectra of a blank Ag powder, Ag (18), and stearic acid

Table 2 Main peak assignments of DRIFTS spectra [13–15]

Chemical	Peak/cm^{-1}	Assignment
	2800–2900	C–H stretching
Stearic acid	1700	C=O stretching in –COOH
	1460	CH_2 bending
	2800–2900	C–H stretching
Ag (18)	1560	asymmetric stretching of –COO$^-$
	1410	symmetric stretching of –COO$^-$

DSC Study of lubricated Ag flakes

DRIFTS results in above section indicated that the fatty acids formed Ag salts with Ag flake surfaces. Since all of these fatty acid have similar behavior, only stearic acid lubricated Ag flake, Ag (18), were selected to conduct further study. For comparison, a mixture of blank Ag powder and Ag stearate (mass ratio of Ag powder to Ag stearate is 99 to 1) was also used in this study. Ag (18) and the mixture were studied by DSC dynamic scan under air and results are shown in Fig. 9. DSC curves of Ag (18), the blank Ag powder, and stearic acid at the temperature range from 130 to 165°C are shown in Fig. 10.

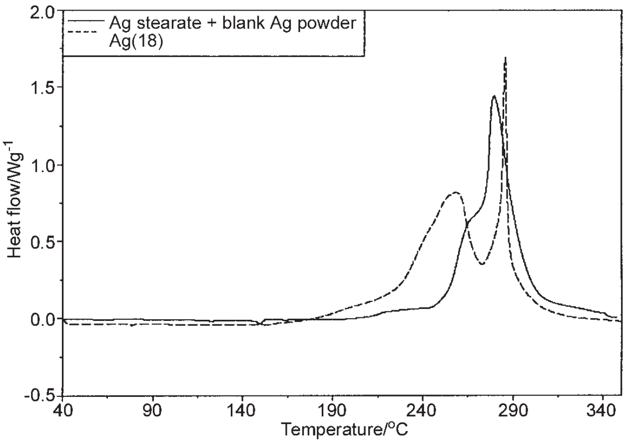


Fig. 9 DSC dynamic scans (in air) of the stearic acid lubricated Ag flake, Ag (18), and a mixture of Ag stearate and a blank Ag powder

As can be seen from Fig. 9, the mixture of Ag stearate and the Ag powder showed a similar exothermic DSC peak as Ag (18). This also indicated that lubricant layer on the Ag (18) was Ag stearate not stearic acid.

In Fig. 10, a small endothermic peak (at approximately 146°C) was found for stearic acid lubricated Ag flake, Ag (18). There was not a peak at this temperature range for stearic acid and the blank Ag powder. The fact that the peak temperature of

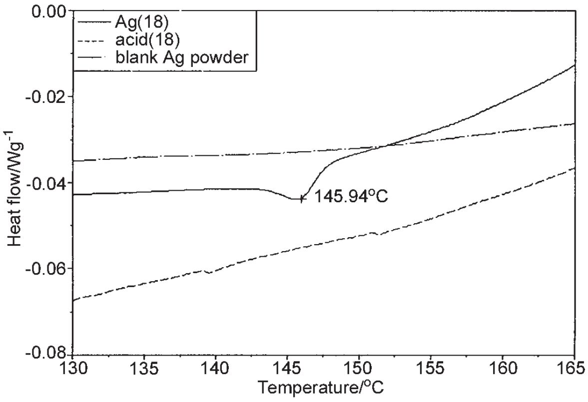


Fig. 10 Dynamic DSC scans of the stearic acid lubricated Ag flake, Ag (18), stearic acid (acid 18), and blank Ag powder

this peak is very close to the melting temperature of Ag stearate further proved that stearic acid on the Ag powder surface formed a salt with Ag surface.

Conclusions

Ag flakes lubricated with longer chained fatty acids (1) showed exothermic DSC peaks at higher temperatures and (2) started to lose mass at higher temperatures than those lubricated with shorter fatty acids. A layer of lubricants stayed on Ag flake surface after lubrication process. The lubricant layer was a salt, rather than a free acid, which was formed between the fatty acid and the Ag flake surface. The exothermic DSC peaks (in air) of a lubricated Ag flake were due to the oxidation of the lubricant layer.

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