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THE USE OF DSC IN PREDICTING LOW TEMPERATURE BEHAVIOUR OF MINERAL OIL PRODUCTS.

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ABSTRACT

Differential Scanning Calorimetry (DSC) has been used to determine the amount and type (identified by crystallization temperature) of paraffin wax (n-alkanes) in mineral oils. Attempts to predict low temperature properties of some mineral oil products like transformer oil and engine oils are presented. A correlation between "Borderline Pumping Temperature" and crystallization of paraffin wax is suggested.

INTRODUCTION

Low temperature properties are very important in certain mineral oil based products designed for outdoor applications, especially if they are to be used in cold climates such as northern Europe, Canada or the northern Soviet Union. These low temperature properties depend on several factors including viscosity, viscosity index, nature of additives or the presence of paraffin wax in the oil. In the early 70's F. Noel[1] and C. Giavarini et al [2] showed that the amount and the crystallization temperature of paraffin wax in mineral oil could be determined by DSC.

The present work will discuss how to use information from DSC curves to predict properties of base oils, transformer oils and engine oils.

METHOD

A DSC analysis begins with a cooling cycle starting at least 50^{o}C above the temperature where crystallization can be expected. The sample is cooled at a rate of 10^{o}C/min to -100^{o}C, immediately followed by heating at a rate of 10^{o}C/min until all paraffin wax is melted. Carefully controlled cooling of the sample is important to obtain a good repeatability since the course of melting can vary with cooling rate.

The temperature at the start of crystallization (T_c, fig 1) is determined at different cooling rates and is then extrapolated to 0^{o}C/min. The super cooling of wax in straight well refined base oils usually falls between 3.5^{o}C and 7^{o}C. In routine analysis a mean value of 5^{o}C is used.

The crystallization peak is integrated and the total amount of crystallized

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wax is calculated using a figure of 43 cal/g as the heat of crystallization, which is a mean value derived from literature. [1,2,3]

This method permits detection of 0.3% paraffin wax in 15 mg sample. The precision is approximately ±20%, mainly due to errors in the figure for heat of crystallization and instrument.

During the heating cycle, the oil must be raised to a higher temperature than the crystallization point to assure complete fusion of the waxes (T_f fig 1). This temperature interval (T_f-T_c) is a critical one since the paraffin wax could be solid or liquid depending on temperature history.

RESULTS AND DISCUSSION

Base oils

Traditionally base oils are divided into paraffinic and naphthenic oils. Intermediate oils also exist. This classification is based on physical properties like density, viscosity index and Watson factor. Typically, paraffinic oils always contain n-alkanes (paraffin wax) which crystallize upon cooling. If they are to be used as base stocks for lubricant manufacturing they always have to be dewaxed. Even after dewaxing they usually contain several percent paraffin wax.

Naphthenic oils contain little or no paraffin wax. In fig 1 two DSC-curves, one from a naphthenic and the other from a dewaxed paraffinic oil are compared.

The difference in content of paraffin wax is typical and could be used for classification of an oil as either naphthenic or paraffinic.

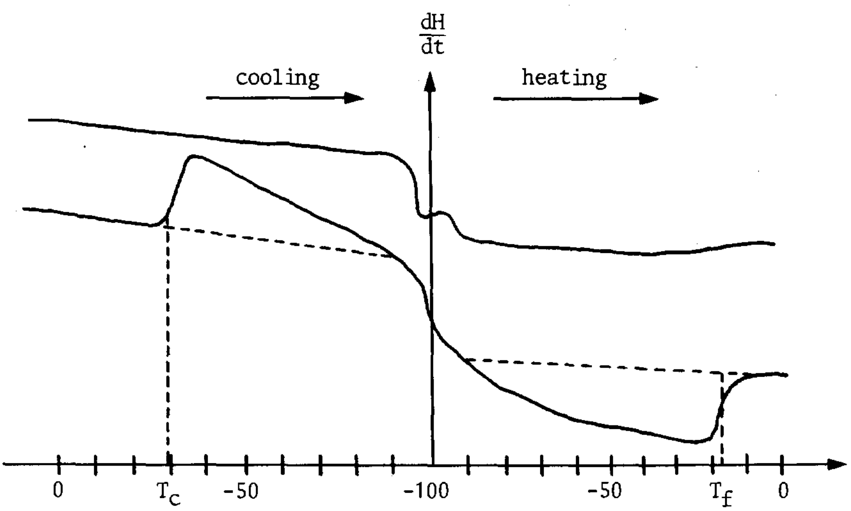

Fig 1. Examples of DSC curves from well refined mineral oils.
Top: Naphthenic oil Bottom: Dewaxed paraffinic oil

The traditional method for analysing the crystallization temperature of wax in oil is Cloud Point ASTM D2500. F. Noel found a very good correlation between the Cloud Point and wax crystallization as measured by DSC[1]. We have made a similar study in which we have used dewaxed well refined paraffinic oils and formulated products with Cloud Points between -5°C and -25°C. The results confirm a correlation, although there is considerable scattering (fig 2). Straight mineral oils and formulated products give a similarly scattered pattern.

Another widely used analysis for low temperature properties is Pour Point (ASTM D97). The Pour Point depends heavily on viscosity and also, in the case of a paraffinic mineral oil, on the shape of wax crystals formed during crystallization. The shape of the crystals can be influenced by polymeric additives (Pour Point depressants). Consequently the Pour Point can be lowered by the addition of a carefully selected Pour Point depressant. On the other hand, the beginning of crystallization cannot be changed by Pour Point depressants.

Transformer oils

The function of an oil in a transformer is to provide electrical insulation and also to cool the transformer. To be able to cool the transformer effectively it must circulate freely throughout all the channels inside the core. If paraffin wax crystallizes in a transformer then there is always a risk of blocking the channels, which may result in a local overheating. With DSC, the crystallization temperature can easily be determined.

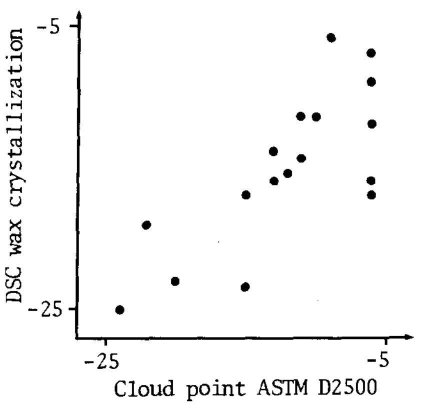

Fig 2. Correlation between DSC and cloud point

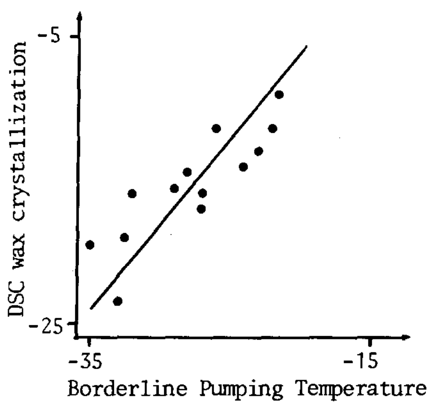

Fig 3. Correlation between onset of wax crystallization as measured by DSC and BPT as measured by MRV

This temperature is the lowest temperature at which a transformer oil should be used even if the Pour Point is lower. If the Pour Point is higher than the crystallization temperature, of course the Pour Point is the lowest recommended temperature to use. This is especially important when naphthenic oils, which lack paraffin wax, are used.

Engine oils

Engine oils are very complex products which contain a large amount of different additives including polymers. There are two widely employed methods for the classification of low temperature properties of engine oils according to SAE: "Cold Cranking Simulator" (CCS) ASTM D2602 and "Mini Rotary Viscometer" (MRV) ASTM D3829. The viscosity as measured by MRV is used to calculate the "Borderline Pumping Temperature" (BPT) defined as the temperature at which the viscosity is 30 Pas. The onset of crystallization as measured by DSC shows a good correlation with BPT as can be seen in fig 3. These findings were unexpected since the low temperature properties depend on several other factors including viscosity of the base oil and the nature of polymeric additives. The results indicate however, that the crystallization of paraffin wax, probably together with polymers, has great influence on the low temperature rheology of an engine oil.

CONCLUSION

DSC is an excellent analytical tool for quantifying and characterizing paraffin wax in mineral oil products. DSC also seems to have a potential to predict low temperature properties of engine oils, although a lot of work remains before a full explanation can be given and generality can be proven.

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