Journal of Thermal Analysis, Vol. 43 (1995) 143-147

INVESTIGATION OF OXIDATION OF MICROCRYSTALLINE PETROLEUM WAX

M. Paczuski, R. Pulawski and F. Tomaszewska

Institute of Chemistry, Warsaw University of Technology, Lukasiewicza 17, PL–09–400 Plock, Poland

Abstract

The processes of oxidation of microcrystalline petroleum (residual) wax were investigated. DSC was applied to estimate the thermal conditions and the influence of selected catalysts on the process. Laboratory tests of oxidation fully confirmed the results of the DSC investigations.

Keywords: DSC, microcrystalline, petroleum wax

Introduction

Residual waxes are obtained in base oil-refining processes when vacuum residues are manufactured. Because of their chemical composition, they have found a variety of uses in the chemical industry. One of the most interesting application of microcrystalline waxes is production of temporary anticorosion products.

Chemical modification of the raw material to produce thin-layer anticorrosion products relies on the introduction of a polar group into the molecule. One of the methods most often applied for modification is oxidation by oxygen, air or ozone, whereby an acid, ester or similar group is incorporated. Physicochemical parameters that indicate chemical changes during oxidation are the acid and ester numbers of the product.

In connection with the temperature of the process, the thermal stability of the raw material was measured by densimetric scanning calorimetry.

Experimental

The thermooxidative stability of the residual petroleum wax was measured with a DuPont model 910 DSC apparatus equipped with a 1090 thermal analyser, using the program 'Oxidative Stability Data Analysis Version 2.0'.

The heat flow (mW) was measured as a function of linearly increasing temperature under the following conditions:

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

- temperature range: 313–573 K (40–400°C);
- rate of temperature increase: 10 deg·min^{-1};
- oxidation gas: oxygen;
- pressure: atmospheric;
- gas flow: 10 cm^3·min^{-1}.

Physicochemical properties of the raw material, residual wax obtained from Gdansk Refinery S.A., are presented in Table 1.

Table 1 Selected physicochemical properties of the residual wax

No	Properties		Validity
1	Molecular mass, g/mole	712	712
2	Melting point, °C	73	73
3	Group composition, %		
	c) naphteno-paraffinic hydrocarbons		78.3
	b) aromatic hydrocarbons		9.6
	c) resins		0.9
4	Saponification number, mg KOH/g	0.4	0.4
5	Acid number, mg KOH/g	0.03	0.03

Results and discussion

DSC curves relating to the oxidation of the microcrystalline wax and the influence of soluble oleates of Mn and Cu are depicted in Figs 1–3.

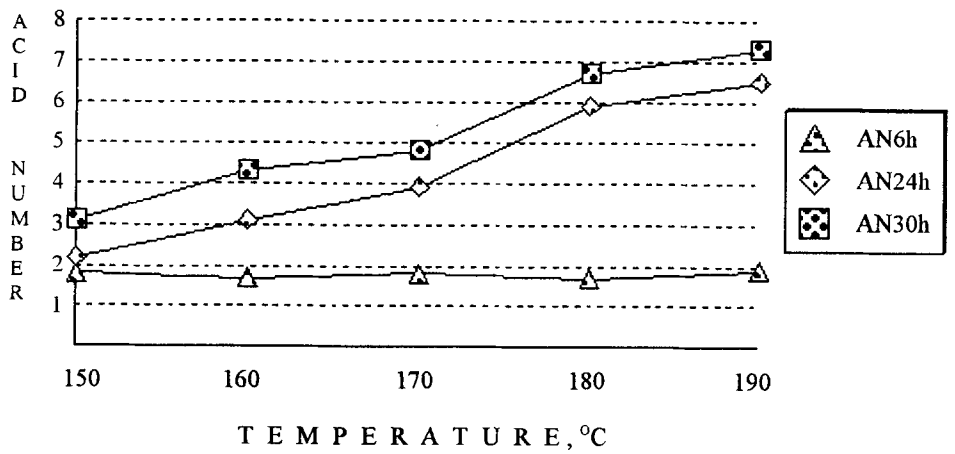

Fig. 1 Acid number of the oxidized raw material as a function of the duration of the process

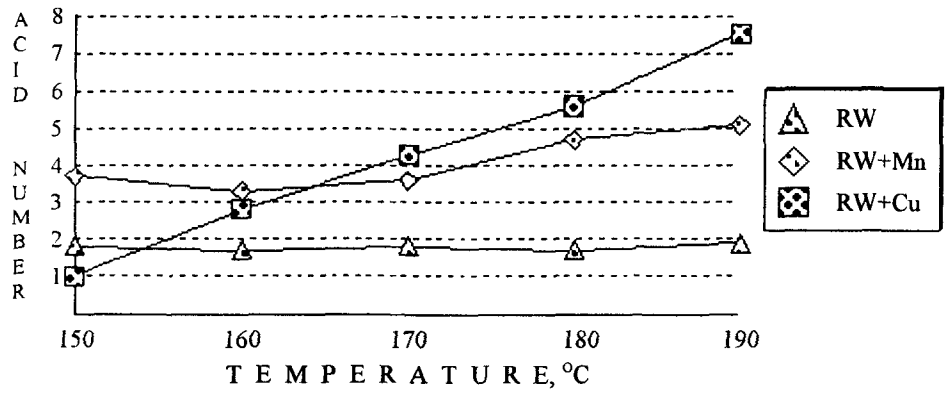

Fig. 2 Acid number of the petroleum wax after oxidation for 6 h without and with addition of catalyst

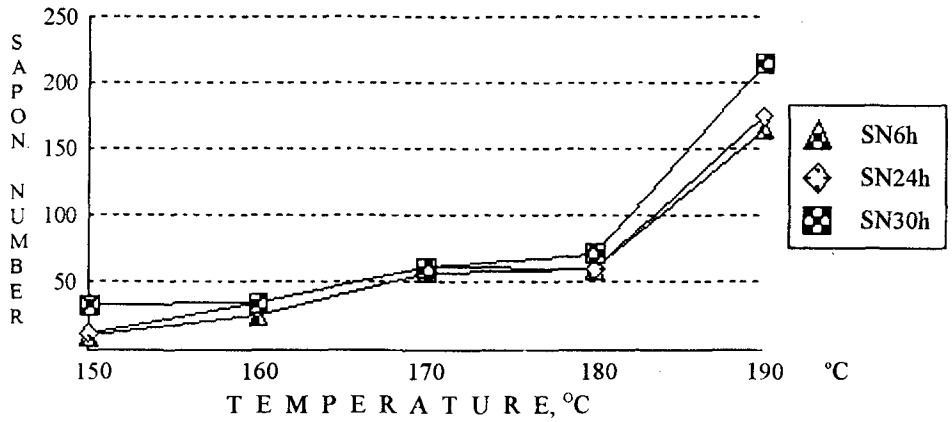

Fig. 3 Saponification number of the petroleum wax oxidized in the presence of Cu-oleate catalyst as a function of the duration of the process

The oxidation of the raw material was characterised by the 'onset' temperature, the extrapolated 'onset' temperature and the temperature of maximum heat flow (Table 2).

Table 2 Characteristic temperatures of the oxidation in DSC investigations

Oxidised material	Onset temp./ °C	Extrapolated onset temp./ °C	Temp. of max. heat flow/ °C
Residual wax (RW)	180	224	300
RW + Mn	124	185	267
RW + Cu	180	225	270

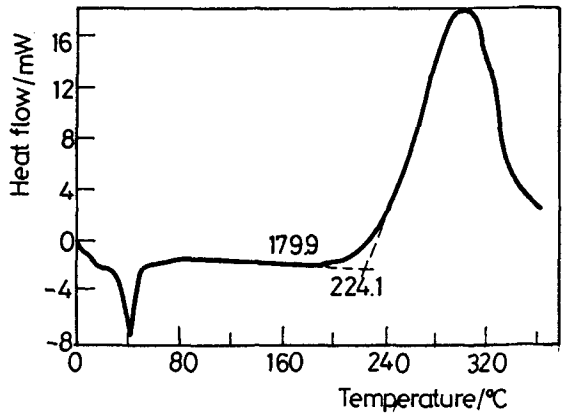

Fig. 4 DSC curve of petroleum wax oxidation

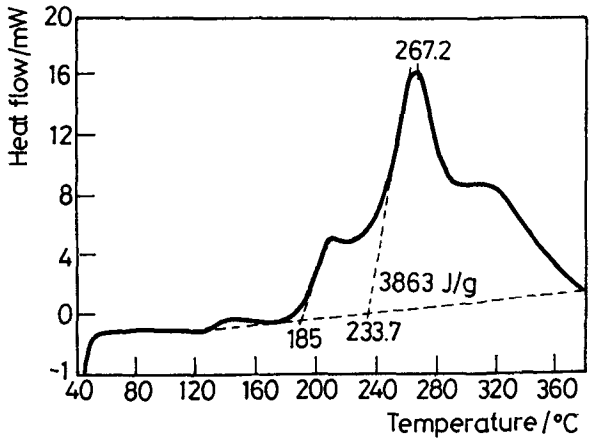

Fig. 5 DSC curve of petroleum wax oxidation in the presence of Mn oleate catalyst

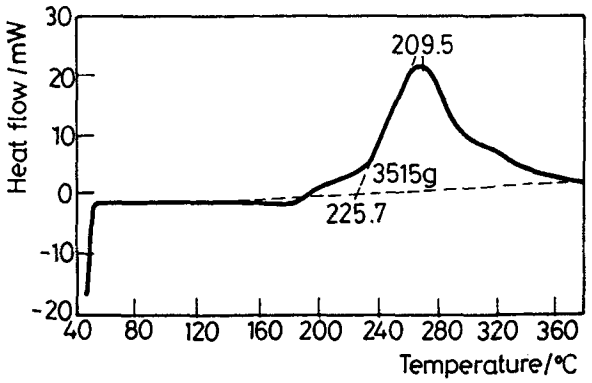

Fig. 6 DSC curve of petroleum wax oxidation in the presence of Cu oleate catalyst

The 'onset' temperature of the residual wax at 180°C indicates the beginning of the oxidation process. Addition of Mn oleate lowers this parameter to 124°C, which shows the strong influence of the catalysts. It means that the process can be carried out under milder conditions.

Both Mn and Cu salts lower the temperature of maximum heat flow.

On the basis of the DSC results, some laboratory experiments on wax oxidation were performed. The results of oxidation with air are shown in Figs 4–6. They confirmed the value of the DSC technique for the investigation of oxidation of petroleum products, establishment of the process conditions and the possibility of catalysis.

Zusammenfassung — Es erfolgte eine Untersuchung der Vorgänge bei der Oxidation von Erdölparaffin (Rückstand). Mittels DSC wurde eine Abschätzung der thermischen Bedingungen und des Einflusses ausgewählter Katalysatoren auf den Vorgang vorgenommen. Durch Labortests der Oxidation wurden die Resultate der DSC-Untersuchungen voll bestätigt.