Journal of Thermal Analysis (1985) 763–770

STUDY OF THERMAL STABILITIES OF SOME HEAT TRANSFER OILS

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(Received July 24, 1984; in revised form, February 22, 1985)

This paper discusses the thermal behaviour and stabilities of some heat transfer fluids. These included four solvent-refined mineral oils, two aromatic extracts and two synthetic oils. Results of this thermoanalytical investigation, which simulated different atmospheric conditions, showed the synthetic oils to have higher thermal stabilities than those of the other oils.

The refined mineral oils exhibited higher thermal stabilities than those of the aromatic extracts when studied under a static air atmosphere. This behaviour was reversed when the experiment was performed under a confined atmosphere of air.

These observations are attributed mainly to the environmental changes and also to the compositions of these products.

The transfer of heat in open and closed systems plays an important part in many manufacturing processes. Typical operations include petroleum refining, chemical synthesis, plywood lamination, plastic production, etc.

Many organic heat transfer oils have been developed and exhibit good heat transfer at elevated temperatures, typically in the 150–300° range. The most common and economical of these organic oils are the petroleum-derived hydrocarbon oils, although synthetic and chlorinated oils too are often used [1].

A heat transfer fluid should be non-corrosive to metals, it should be liquid over a wide temperature range and in general it should have a low vapour pressure. Such a fluid should be applicable as a heat transfer medium over an extended period of time at a given temperature, and should exhibit a high thermal stability. Thus, a heat transfer fluid is often required to operate at temperatures of the order of 250° or higher over long periods [1].

Thermal properties of oils are usually assessed by measuring changes in stability, viscosity, density, or the formation of insoluble material. Regardless of how the process is studied, it involves a change in the energy of the material in question [2].

Recently, however, thermoanalytical techniques such as differential thermal analysis, differential scanning calorimetry, thermogravimetry and derivative

John Wiley & Sons, Limited, Chichester
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thermogravimetry, which are instrumental methods wherein the sensing devices respond to temperature changes caused by energy changes within the material, have been used extensively as simple and quick methods for studying the thermal stabilities of petroleum-derived products such as lubricating oils, greases and bitumens [3–5].

The work presented in this paper deals with study of the thermal stabilities of some petroleum-derived and synthetic heat transfer fluids. The stabilities of the oils toward oxidative degradation were investigated using differential scanning calorimetry. Thermal behaviour under a confined atmosphere of air was studied in the special cell of the differential thermal analyser, while weight loss on increase in temperature under an inert atmosphere was measured thermogravimetrically.

Experimental

Differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetry (TG) and derivative thermogravimetry (DTG) were all carried out on a Heraeus TA 500 thermal analyser.

Additive-free, grade 40 base stock, grade 60 high viscosity index (HVI), grade 60 low viscosity index (LVI), grade 150 base stock, grade 40 aromatic extract, grade 60 aromatic extract and diphyl (synthetic oil) were all obtained from a local refinery.

Table 1 Properties of the additive-free heat transfer oils

Oil	Density at 20°C	Refractive index, 20°C	Viscosity cSt at 40°C	Sulfur wt., %	Mono- wt., %	Di- wt., %	Tri- aromatics & polar cpds.
Silicone	1.05	1.5040	70.5	—	—	—	—
Diphyl	1.06	1.5105	75.0	—	—	—	—
Grade 40 stock	0.866	1.4785	40.5	0.19	5.4	3.6	—
Grade 60 HVI	0.870	1.4855	58.0	0.45	12.6	8.5	0.92
Grade 60 LVI	0.886	1.4899	101.5	1.1	13.2	10.5	3.5
Grade 150 stock	0.893	1.4958	148.0	0.9	12.0	9.5	1.2
Grade 40 extract	0.868	1.4823	30.3	0.35	29.5	25.0	20.5
Grade 60 extract	1.08	1.5698	155.5	4.31	20.0	34.5	25

Aromatic fractions were separated chromatographically on a silica-gel column using selective solvents.

The silicone oil was purchased from Aldrich Chemical Company Ltd. Data on the oils are given in Table 1. Pure benzoic acid and tin were used to calibrate the thermal analyser.

In the DSC measurements, oil samples weighing 20 mg were heated at a rate of 10 degree/min in an aluminium crucible under a static air atmosphere. The reference cell was left empty.

DTA measurements were carried out using the special purpose cell. Samples of oil 25–30 mg were placed in glass ampoules and sealed 1 cm above the oil. A similar, empty ampoule was sealed and placed in the same cell as a reference. The temperature sensing was performed on the outside of the ampoules. The measuring cell was then placed in a silver block, which ensured even temperature distribution.

TG and DTG curves were recorded simultaneously by placing a sample weighing 10–12 mg in a platinum crucible and heating at a rate of 20 degree/min under an atmosphere of nitrogen gas flowing at a rate of 10–15 dm^3/h.

Results and discussion

Thermal degradation under a static atmosphere

Differential scanning calorimetry was used to determine the thermal stabilities of different types of oils. When a sample of oil was heated in air, the DSC apparatus recorded an exothermic effect resulting from the oxidative degradation of the oil. The onset temperature of the exotherm was taken as a measure of the thermal stability of the oil; the higher the onset temperature of the exothermic reaction, the more the oil is resistant towards oxidative degradation, and conversely [3, 4].

The onset temperature of the exothermic effect is usually estimated from the intersection of the tangents extrapolated to the DSC trace, as described earlier [6–9]. The DSC signals of the eight types of heat transfer oils between room temperature and the onset of the exothermic effect are displayed in Fig. 1.

It is obvious from Fig. 1 that the diphyl and silicone oils possessed the highest onset temperatures of oxidative degradation, at 275 and 265°, respectively, indicating the high thermal stabilities of these synthetic oils.

The grade 60 HVI and grade 150 oils exhibited higher onset temperatures of oxidative degradation (190 and 200°) than that of the grade 40 oil (180°). One of the reasons for this behaviour is the presence of tri-aromatic and polar compounds ($>0.9\%$) in the two former oils, which are well known to act as natural oxidation inhibitors [10, 11]. This was confirmed by evaluating the onset temperature of the 60 HVI oil of the same grade which had been subjected to contact treatment with small amounts of silica gel, which led to the removal of 0.4% of the tri-aromatics and polar compounds while the other aromatic fractions remained unchanged. The onset temperature of the oil decreased by 9° to 186°. The onset temperature (179°) for the grade 40 oil which had been subjected to silica gel treatment to remove 4% of its mono and di-aromatic constituents was almost the same as that of the untreated oil (180°). Although the grade 60 LVI is richer in tri-aromatic, polar and sulphur compounds and showed an onset temp. of 240°, it exhibited a faster rate of oxidation, indicating that higher contents of these compounds could impart a degradative effect to the oils [8, 10, 11].

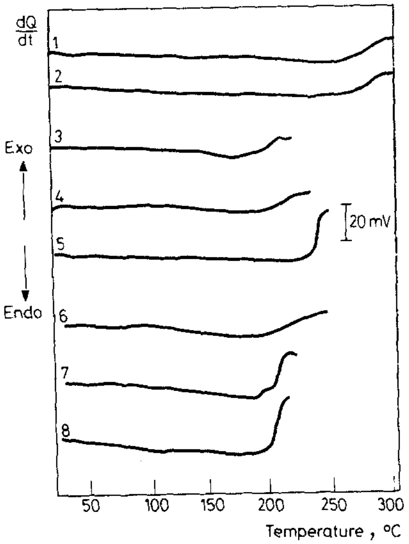

Fig. 1 DSC traces of 1, silicon oil; 2, diphyl oil; 3, grade 40 base oil; 4, grade 60 HVI; 5, grade 60 LVI; 6, grade 150 base oil; 7, grade 40 aromatic extract and 8, grade 60 aromatic extract

The grade 40 and 60 aromatic extracts, which contain more than 20% tri-aromatic and polar compounds, exhibited onset temperatures of oxidative degradation almost the same as those of the grade 60 HVI and 150 oils, i.e. 205 and 204°, respectively. However, once degradation commenced, the exothermal reaction proceeded at a very fast rate.

The thermal stabilities of these heat transfer oils are clearly governed by their compositions. However, the situation in the DSC measurements, e.g. a large surface area of contact and an excess volume of surrounding air atmosphere, must also have major influences on the behaviour of these oils during thermal degradation.

Thermal degradation under a confined atmosphere

Differential thermal analysis was also used to study the thermal degradation of the heat transfer oils under confined atmospheres. The DTA traces of the eight types of heat transfer oils are shown in Fig. 2.

The diphyl and silicone oils exhibited slight endothermic changes, starting at about 280–290°, due to evaporation with no degradation up to 350°. These initial temperatures are close to the initial temperatures of transition in the TG curves of the diphyl and silicone oils, which were 300 and 280°, respectively.

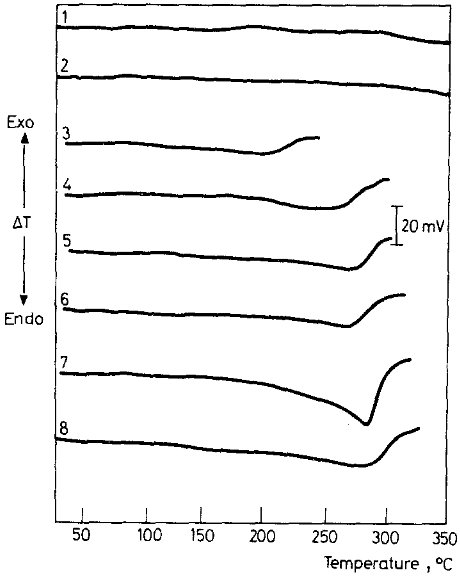

Fig. 2 DTA traces of 1, silicon oil; 2, diphyl oil; 3, grade 40 base oil; 4, grade 60 HVI; 5, grade 60 LVI; 6, grade 150 base oil; 7, grade 40 aromatic extract and 8, grade 60 aromatic extract

The grade 60 HVI, 60 LVI and 150 base stock oils showed a similar pattern of behaviour, with an endothermic change commencing at 200–250°, due to evaporation prior to degradation, which started at about 270°. The corresponding initial temperatures of transition in the thermogravimetric curves for these oils were 200, 230 and 265°, respectively. The grade 40 oil was the least thermally stable of the solvent-refined oils, with an onset temperature of degradation of 210°.

Both aromatic extracts, i.e. the grade 40 and 60, possessed onset temperatures about 15° higher than the former three solvent-refined mineral oils (60 HVI, 60 LVI and grade 150 base oil). However, evaporation for the grade 40 extract, which started at about 170°, was more pronounced than for the other heat transfer oils and the corresponding initial temperature of transition in the TG curve of this particular extract was 190°.

In the DTA measurements, the thermal stabilities of the heat transfer oils are clearly governed by the limited air atmosphere confined in the sample container, i.e. the sealed glass ampoule.

Thermogravimetric degradation under an inert atmosphere

TG and DTG curves of the heat transfer oils were recorded between room temperature and 600°.

The transition temperatures of the oils and their relative weight losses are given in Table 2. The weight losses under an inert atmosphere of nitrogen correspond mainly to their volatilization.

The grade 40 oil and 40 extract had the lowest onset temperatures of transition, 180 and 190°, while the diphyl, silicone and grade 150 oil possessed the highest temperatures of transition, 300, 280 and 265, respectively. This trend in behaviour is related to the increase in the average molecular weight of these oils, displayed in the same Table.

Table 2 Transition temperatures of the heat transfer oils and their relative weight losses (average of two determinations)

Oil	Average molecular weight	T_1, °C	T_{max}	T_2	wt. loss, %
Silicone	> 10,000	280	490	530	99.1
Diphyl	> 10,000	300	500	550	99.0
Grade 40 Oil	340	180	275	327	99.6
Grade 60 HVI	425	200	385	425	99.5
Grade 60 LVI	480	230	360	437	99.2
Grade 150 stock	675	265	490	537	99.2
Grade 40 extract	380	190	290	350	99.0
Grade 60 extract	475	220	400	450	98.8

T_1: initial temperature of transition.
T_{max}: maximum temperature of transition.
T_2: final temperature of transition.
wt. loss, %: the weight loss involved in the transition.

The results suggested that the sequence of thermal stabilities of the different heat transfer oils under a static air atmosphere is as follows:

synthetic oils > solvent-refined mineral oils > aromatic extracts

while the sequence under a confined atmosphere of air is:

synthetic oils > aromatic extracts > solvent-refined mineral oils

However, the choise of these oils for a particular application is also dependent on the design of the process and on economic factors.

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Zusammenfassung — Das thermische Verhalten und die Stabilität einiger Wärmeübertragungsflüssigkeiten werden diskutiert. Die Untersuchung erstreckt sich auf vier mit Lösungsmittel raffinierte Mineralöle, zwei Aromatenextrakte und zwei synthetische Öle. Aus den Ergebnissen thermoanalytischer Untersuchungen, bei denen verschiedene atmosphärische Bedingungen simuliert wurden, folgt, daß die synthetischen Öle ein höhere thermische Stabilität als die anderen Öle aufweisen. In statischer Luftatmosphäre ist die thermische Stabilität der raffinierten Mineralöle höher als die der Aromatenextrakte. In einer limitierten Luftatmosphäre kehrt sich dagegen dieses Verhalten um. Diese Beobachtungen werden hauptsächlich Veränderungen in der Umgebung und der Zusammensetzung dieser Produkte zugeschrieben.

Резюме — Обсуждено термическое поведение и устойчивость некоторых жидких теплоносителей: четырех селективно-очищенных минеральных масел, двух ароматических экстрактов и двух синтетических масел. Термоаналитические исследования, проведенные в различных атмосферных условиях, показали большую термоустойчивость синтетических масел по сравнению с другими маслами. Очищенные минеральные масла, исследованные в статической атмосфере воздуха, показали более высокую термоустойчивость по сравнению с ароматическими экстрактами. В случае же исследований, проведенных в закрытой атмосфере воздуха, наблюдался обратный эффект. Установленные факты вызваны, главным образом, изменениями окружающей среды и состава исследованных продуктов.