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Note

A THERMAL METHOD FOR DETERMINING THE OXIDATION—AUTOIGNITION CHARACTERISTICS OF OILS

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A laboratory thermal method was needed to determine the oxidation and autoignition characteristics of oils on insulating materials. The desired test method was one that would simulate conditions in chemical and petroleum processing plants where the potential exists for heat transfer oils to come in contact with pipe insulation by spillage or leakage. In the present communication, we are reporting a TGA technique for comparing the weight loss of samples when heated in nitrogen, air, and oxygen atmospheres. The temperature of initial oxidation is readily seen from both weight loss and derivative curves. Autoignition is observed and correlated with these changes.

EXPERIMENTAL

The samples used for this study were prepared by mixing powdered calcium silicate industry-type pipe insulation (Johns-Manville Thermo-12) with the heat transfer oil to be tested. The powdered insulation was screened through a 20-mesh screen to remove any fibers. A mixture of 1 part insulation and 2 parts oil provided a slightly tacky product ideal for laboratory study. Fifty mg of the mixture were placed in a platinum pan equipped with a bucket-type support wire which was attached to the quartz rod of a DuPont 951 TGA. A DuPont 990 thermal analyzer was used as the control device. The thermocouple was placed directly above and adjacent to the sample. The small end of the furnace tube was removed to allow the sweep gas to exit the furnace tube without restriction. This was necessary when autoignition occurred. A purge gas (nitrogen, air, or oxygen) flow of 50 ml min^{-1} and a heating rate of 50°C min^{-1} were used in all experiments. The volatility curves have units of 1—100% weight loss and the derivative curves 1 mg min^{-1} in^{-1}.

RESULTS AND DISCUSSION

Five oils, A—E, were selected for evaluation. Samples A—C are low volatility petroleum-base oils which could be considered as candidate heat transfer oils. Samples D and E are commercially available heat transfer oils. The rela-

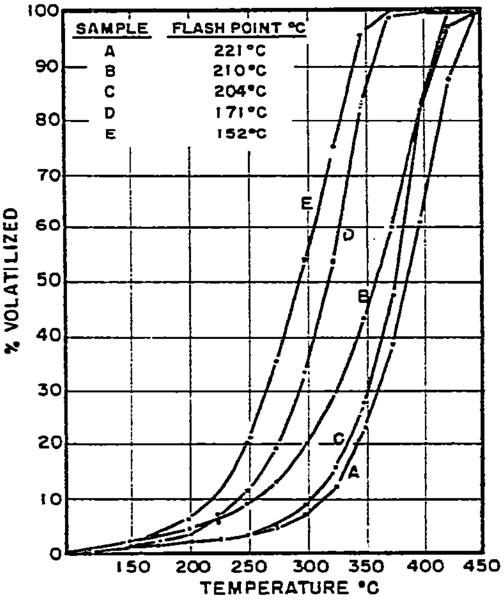

Fig. 1. Volatility curves for samples A, B, C, D, and E normalized to 100%.

tive volatilities and flash points of these oils are shown in Fig 1. The relative volatilities and flash points correlate except for samples B and C but they have no direct relationship to the oxidation or autoignition characteristics of the sample.

The volatility (weight loss) and derivative curves were obtained for samples A, B, and C using nitrogen, air, and oxygen sweep gases. Data are shown in Figs. 2 and 3. Using nitrogen, smooth volatility and derivative curves were obtained for all three samples. Oxidation was observed when the samples were heated in air or oxygen by a rapid increase in temperature in the volatility curve and a deviation from symmetry of the derivative curve. Oxidation

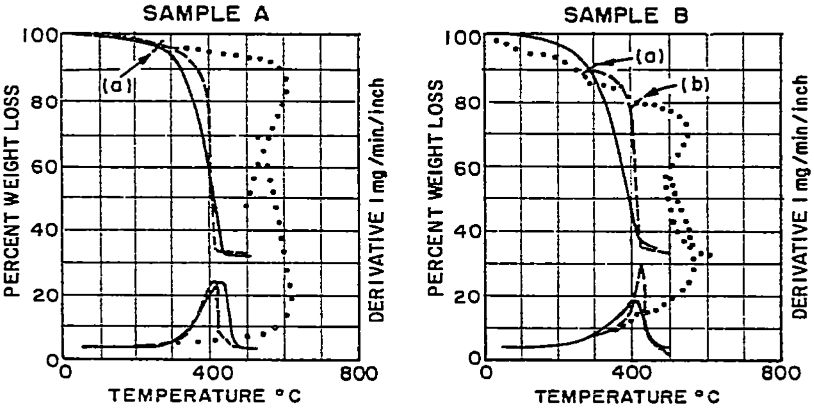

Fig. 2. Weight loss and derivative curves for samples A and B. Sample A: (a) is the initial oxidation point in both air and oxygen and the autoignition point in oxygen. Sample B: (a) is the initial oxidation point in both air and oxygen, and (b) is the autoignition point in oxygen.

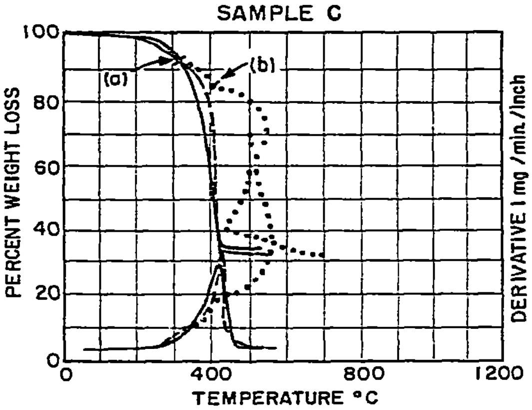

Fig. 3. Weight loss and derivative curves for sample C. Sample C: (a) is the oxidation point in air and oxygen, and (b) is the ignition point in oxygen. (———) Nitrogen; (- - - - -) air; (· · · · · ·) oxygen.

began at 290, 295, and 305° C in air and at 270, 295, and 305° C in oxygen for samples A, B, and C, respectively. Autoignition (evidenced from the autoignition sound) did not occur for samples A, B, or C with air. Autoignition occurred at 270, 420, and 410° C, respectively, for samples A, B, and C using oxygen sweep gas. The normal shape of the derivative curve is greatly altered when rapid oxidation and autoignition occur.

The effects of similar treatment of the more volatile samples, D and E, with the same three sweep gases are shown in Fig. 4. The volatility and derivative curves obtained in nitrogen are smooth for both samples. The volatility curve for sample D, obtained in air, appears to be smooth, but a small amount of oxidation has occurred, as evidenced by the narrow and slightly distorted derivative curve. Small exotherms at 320 and 340° C are shown in the volatility curve of sample D (and displayed vividly with the derivative curve) in oxygen. Autoignition did not occur with this sample. There is no apparent difference in the volatility curves with the three sweep gases for sample D. The back side of the oxygen derivative curve (390° C) is slightly distorted, indicating slight oxidation.

TABLE 1

Tabulation of data for samples A, B, C, D, and E

Sample	Volatility	Temperature (°C)			Assigned rating
		Flash point	Initial oxidation	Auto-ignition	
A	5 (least)	221	290	270	5 Worst
B	3	210	295	420	4
C	4	204	305	410	3
D	2	171	320	None	2
E	1 (most)	152	390	None	1 Best

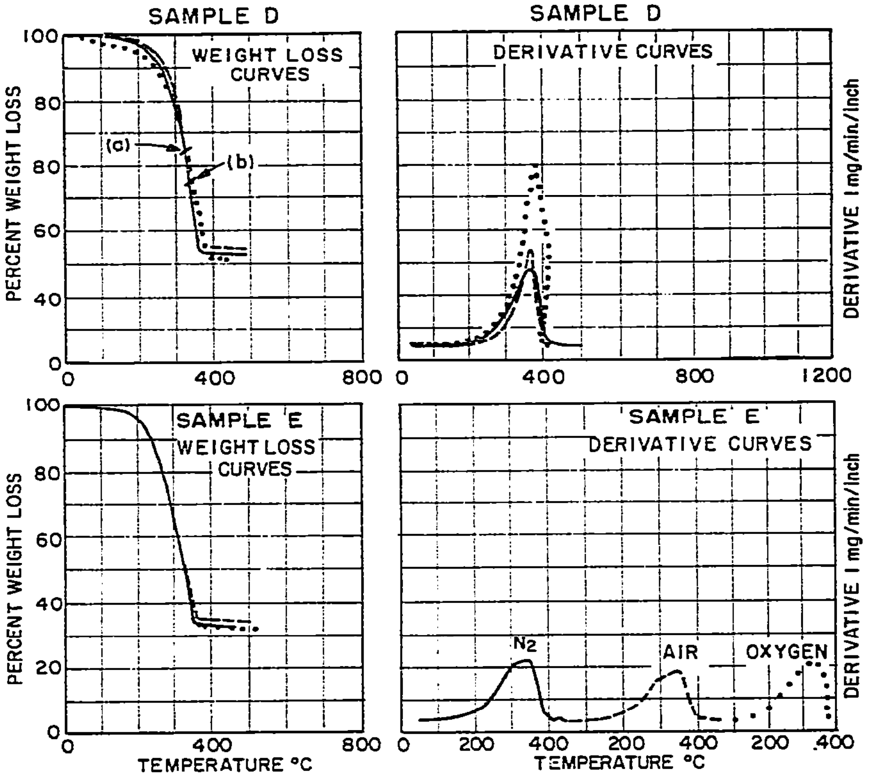

Fig. 4. Weight loss and derivative curves for samples D and E. For sample D, two oxidation points (a) and (b) are shown. Ignition did not occur with either samples D or E, and no oxidation point was found for sample E.

The data relating to the five samples are summarized in Table 1. The volatility is directly related to the flash point, and the flash point is inversely related to the initial oxidation. The initial oxidation for samples D and E is small. Autoignition is directly related to the initial oxidation for samples A, B, and C, but does not occur for samples D and E. The last column in Table 1 shows the assigned ratings given to five samples based on the initial oxidation and autoignition temperatures where a rating of 1 is the best and 5 is the worst. From these data, we conclude that sample E is the best and a desirable heat transfer oil. Sample D is the next best and is also a desirable heat transfer oil. Samples C, B, and A are undesirable for use as heat transfer oils. Table 1 shows that the initial oxidation temperature increases progressively from 290° C for sample A to 390° C for sample E.

The oxidation exotherms are large, and the resulting temperature build-up is very rapid for samples A, B, and C. This is not the case for samples D and E. Here the amount of oxidation is small, and consequently, the amount of heat build-up in the insulation from oxidation is small. The autoignition of samples A, B, and C is directly related to the heat build-up in the insulation. This heat build-up then leads to autoignition.

CONCLUSIONS

The data presented in this paper show that a new test method has been introduced for evaluating and comparing various oils for their oxidation and autoignition characteristics. The test method employs a commercial insulation wetted with the oil, a condition similar to that which could occur in a real plant situation. The method is rapid and reproducible and offers advantages over known literature procedures [1,2]. Oils used in processing plants have been studied using this technique and the laboratory results have been used in oil selection.

REFERENCES

1 P.E. MacDermott, Pet. Rev., 30 (1976) 432.
2 C.G. Wall, Lubr. Eng., 32 (1976) 411.