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Factors affecting oxidation properties in differential scanning calorimetric studies [1]

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Abstract

Fundamental knowledge of the oxidative properties of commercial oils is necessary to predict the stability of these fluids. There is an industry-wide need for a hydrocarbon reference fluid that can be used to establish oxidation properties of motor oils, greases, diesel oils, transmission fluids and vegetable oils. A primary tool to determine the oxidation of oils is differential scanning calorimetry (DSC) or pressure DSC.

A diluted passenger-car motor oil was used to establish an experimentally designed relationship between the variables and the oxidation induction time (OIT) by DSC or PDSC. The variables used for developing this protocol were temperature, pressure, heating rate, sample mass, gas flow rate, and gas type, air or oxygen.

The DSC pan metallurgy played a significant role in the measured OIT. Statistical quality control charting of the oxidation properties focused on a special cause, out-of-control problem that was related to the impurities in the aluminum pans. Iron impurities caused a decrease in OIT of the reference oil. Increasing concentrations of chromium, probably as chromium oxide, stabilized the oxidation process.

INTRODUCTION

There is a need for a hydrocarbon reference fluid with known oxidation properties. A number of researchers have investigated the use of pressure differential scanning calorimetry (PDSC) and differential scanning calorimetry (DSC) as analytical tools to evaluate the oxidation of motor oils, greases and hydrocarbon fluids [1–7]. There are DSC and PDSC test methods for characterizing passenger-car motor oils, base oils, greases, marine diesel oils, synthetic fluids and vegetable oils [8].

A diluted formally-formulated motor oil was used to establish an experimentally designed relationship between the variables and oxidation

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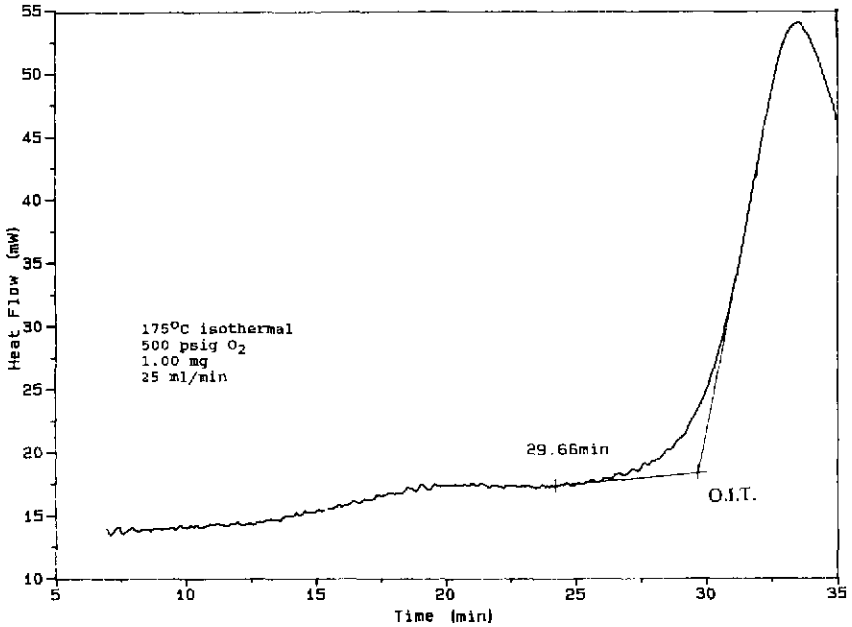

Fig. 1. Oxidation induction time, extrapolated onset time.

properties, i.e. the oxidation induction time (OIT), the isothermal extrapolated onset time (Fig. 1). The dependent variables for developing an oxidation method include: temperature, pressure, heating rate, sample mass, gas flow rate and gas type (air or oxygen). It was found that DSC pan impurities had an effect on the OIT. Scanning electron micrographs (SEM) and energy dispersive X-ray analysis (EDS) of the pans provide the basis for understanding changes in the OIT.

Statistical process control of a PDSC oxdiation test focused on an out-of-control process, with pan metallurgy being the special cause. Iron impurities in the aluminum pans caused a decrease in oxidation stability of the reference oil. Increasing amounts of chromium impurities, probably as chromium oxide, stabilized the oxidation process.

EXPERIMENTAL

The reference oil used in this study was a diluted motor oil that has been well-characterized in our laboratory. It is identified as "Reference Oil A" and contains antioxidants. The sample's flash point was 110°C and its specific gravity at 100°C was 15 cSt.

Factorial designed experiments, 2^3 and 2^4, were used to evaluate the following DSC parameters: gas flow rate, gas flow direction, sample mass, pan type (surface metallurgy), pressure and temperature. The specific experimental conditions are described in Table 1.

TABLE 1

PDSC/DSC experimental conditions

Sample size: 1.00 or 3.00 (±0.1) mg
Gas flow rate: 25.0 or 100 (±1) ml min^{-1}
Pressure: 80 or 500 (±25) psig
Heating: ambient to 175°C or 195°C at 40°C min^{-1}
Temperature: 175°C or 195°C (±0.2°C)
Pan type: aluminum or anodized aluminum

A TA Instruments Inc. PDSC was used at ambient pressure (air and oxygen) as well as at 500 psig applied pressure. The calorimetric evaluation of the specimen was isothermally controlled at temperatures from 175 to 195°C (±0.2°C). Air and oxygen were of high purity (>99.99%) and the gas flow rate was 25 ml min^{-1} through the DSC cell. A variety of pans have been used for OIT experiments including an aluminum hermetic pan, an aluminum solid fat index (SFI) pan and a standard flat-bottom aluminum pan, as well as gold and copper pans. This study discusses only the studies for standard flat aluminum pans and anodized aluminum hermetic pans.

A scanning electron microscope with an energy dispersive X-ray (EDS) spectrometer was used to characterize the DSC metallic pan surfaces.

RESULTS AND DISCUSSION

Temperature has the most pronounced effect on OIT. Increasing the temperature by 20°C will change (decrease) the OIT drastically (Fig. 2). Based on limiting the total OIT to 60 min or less, the optimum isothermal oxidation test temperature for Reference Oil A was 175°C. At this temperature the extrapolated onset time was 30 min, while the peak exothermic time was 34 min.

Altering the pressure within the DSC cell also changes the OIT greatly. The OIT changed from 20 to 7.5 min when the pressure was changed from atmospheric to 500 psig under an oxygen atmosphere (Fig. 3).

An experimentally designed OIT DSC test was devised to investigate the effects of temperature, pressure, sample mass, gas flow rate, gas flow direction and pan type. A 2^3 factorial design was initially developed for pressure (100–500 psig), gas flow rate (25–100 ml min^{-1}) and pan type (aluminum and anodized aluminum). The design is illustrated in Fig. 4. Dot plots of the factor effects in two experiments of this design (Fig. 5) indicate that pressure and gas flow rate are minor contributors to changes in OIT values, but the pan type (metallurgy) has a pronounced effect.

A second experimental design (2^4 factorial) was instituted to study the

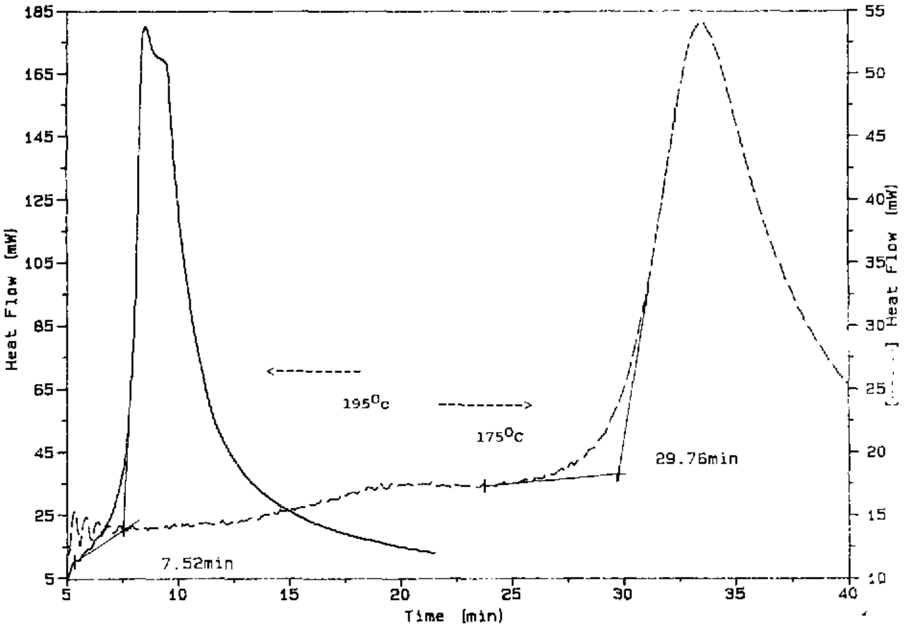

Fig. 2. Temperature effect on OIT at 500 psig O_2.

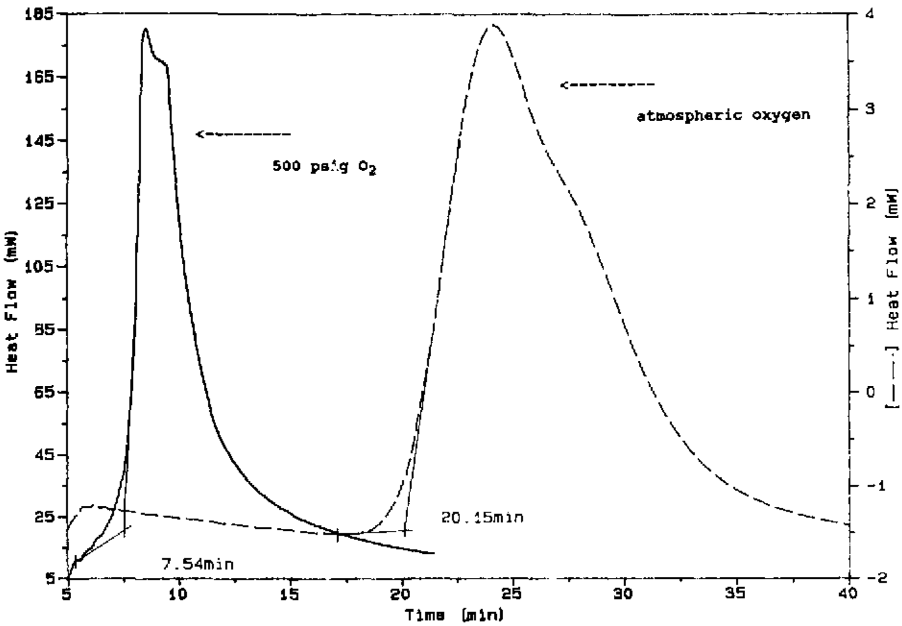

Fig. 3. Pressure effect on OIT are 195°C, isothermal.

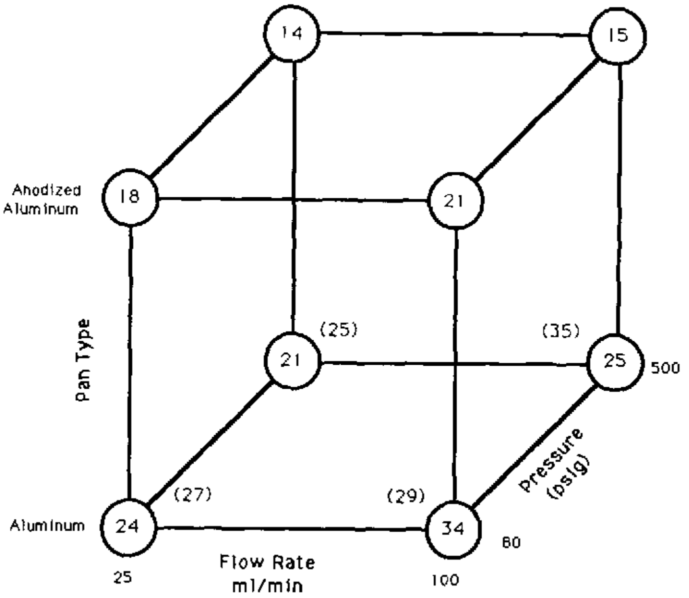

Fig. 4. 2^3 Factorial design for OIT by DSC; repeated values in parentheses.

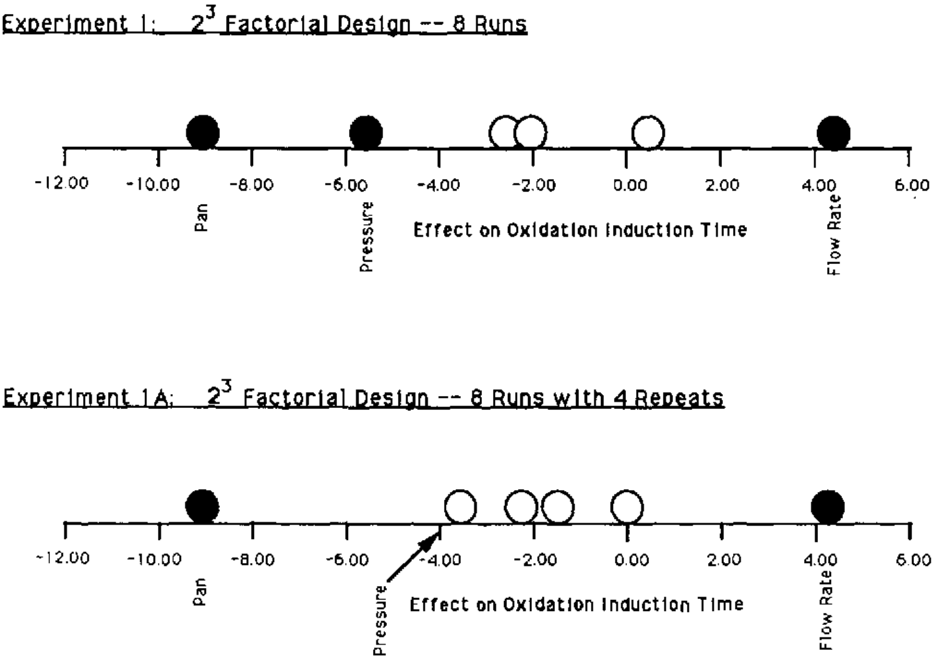

Fig. 5. Dot plot for 2^3 factorial design.

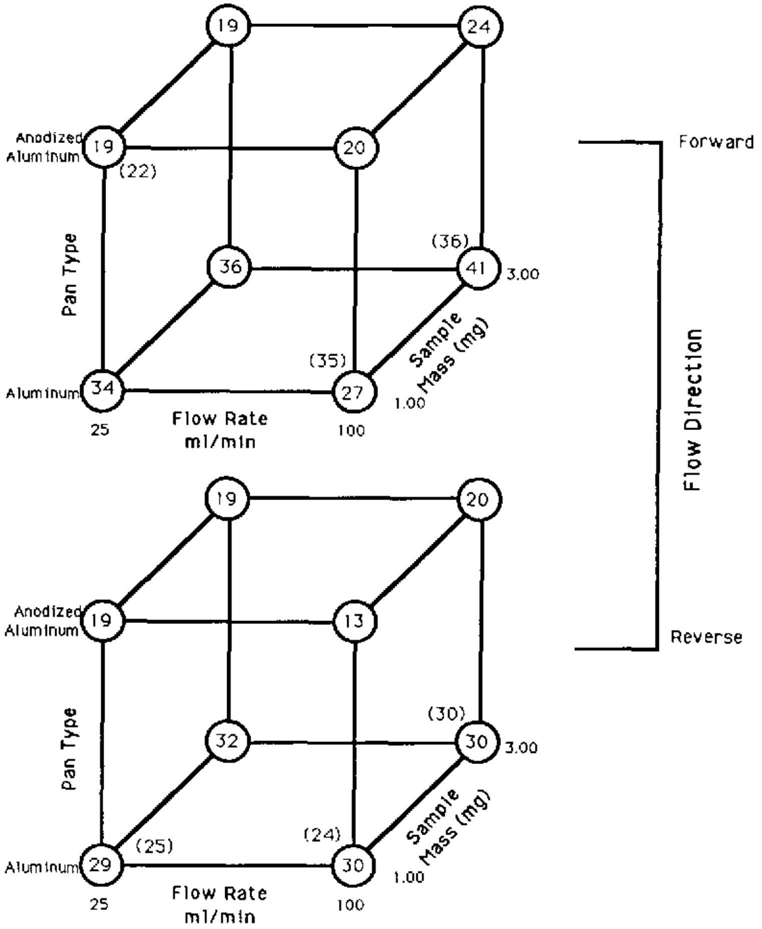

Fig. 6. 2^4 Factorial design for OIT by DSC; repeated values in parentheses.

effects of sample mass and gas flow direction while still examining the effects of gas flow rate and pan type (Fig. 6). A second dot plot (Fig. 7) illustrates the results of this experiment. Sample mass and gas flow direction had minor effects, but the pan metallurgy again had a drastic influence on OIT.

The exothermic peak height of the reference oil was monitored over a four month period. A statistical process control chart was constructed where the exothermic height more than doubled and the process was out of control as shown in Fig. 8. SEM and EDS analyses of the pans revealed impurities of iron, copper and chromium in the aluminum pans (Figs. 9–12). New pans from another source were also monitored by the SEM/EDS techniques. When the iron/chronium ratio was approximately 3.0, the oxidation pocess was out of control (Table 2). The aluminum pans with an iron/chromium ratio of approximately 1.3 brought the oxidation test back

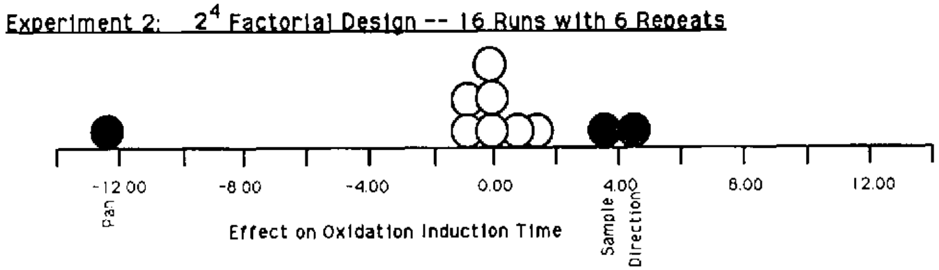

Fig. 7. Dot plot for 2^4 factorial design.

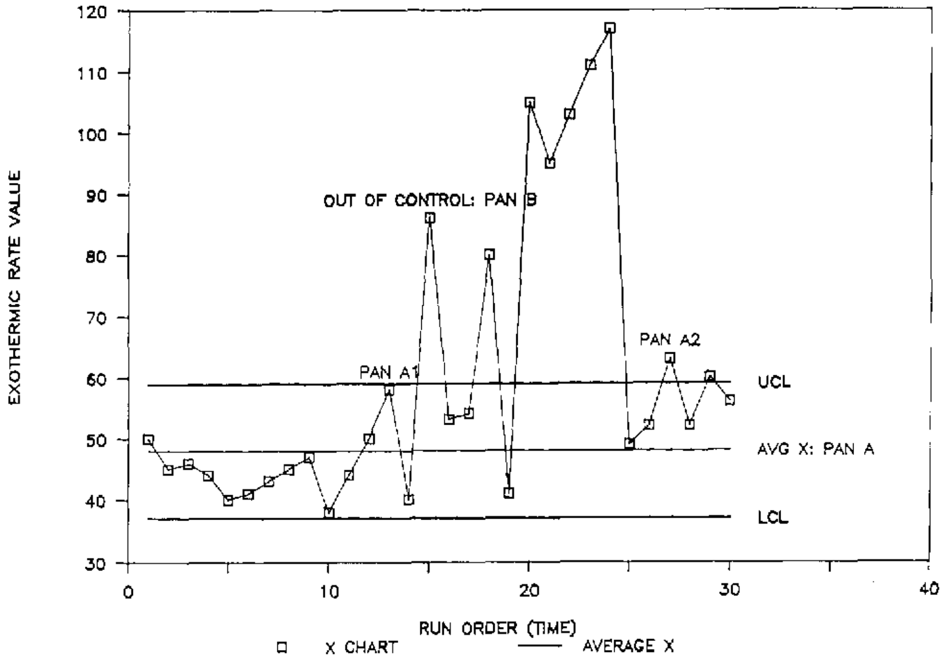

Fig. 8. Control chart for OIT studies.

into control. The DSC/PDSC optimum oxidation test conditions with Reference Oil A are given in Table 3. The anodized aluminum pans are recommended for further oxidation tests. (Suitable pans are manufactured by TA Instruments, Inc. New Castle, DE, USA.)

CONCLUSIONS

When the isothermal oxidation temperature of the Reference Oil A increased, the OIT decreased. Increasing the applied pressure from 14.5 psi to 500 psig oxygen or air also decreased the OIT. In our laboratory, the OIT value was repeatable.

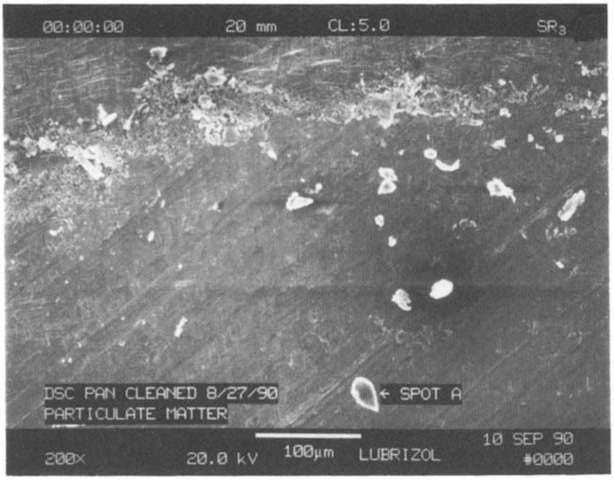

Fig. 9. SEM of anodized aluminum pan (empty).

However, OIT varied with the commercial pan metallurgy. The OIT of Reference Oil A in anodized aluminum pans was statistically lower and more repeatable than the OIT value measured in the standard aluminum pan. Statistical process control (SPC) of the oxidation peak height of Reference Oil A revealed a special cause problem. An out-of-control process was related to residual iron and chronium in the aluminum pan even with rigorous pan cleaning with organic solvents. Elemental impurities in the aluminum pans were identified by SEM/EDS. A given supply of pans caused the DSC oxidation peak height to more than double. When special cause aluminum pans were replaced with new aluminum pans from a different source, the system was brought under control.

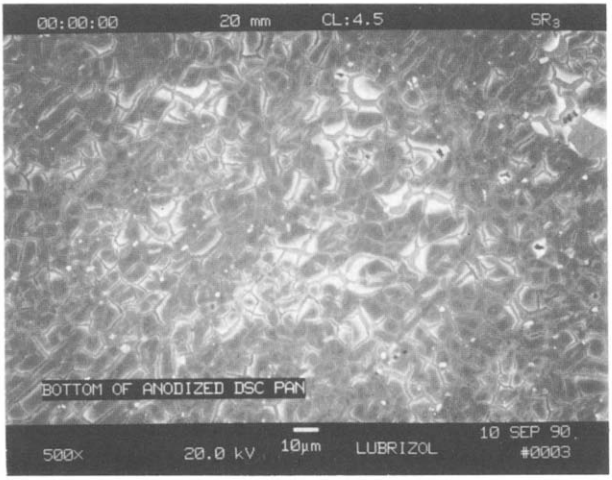

Fig. 10. SEM of aluminum pan (empty).

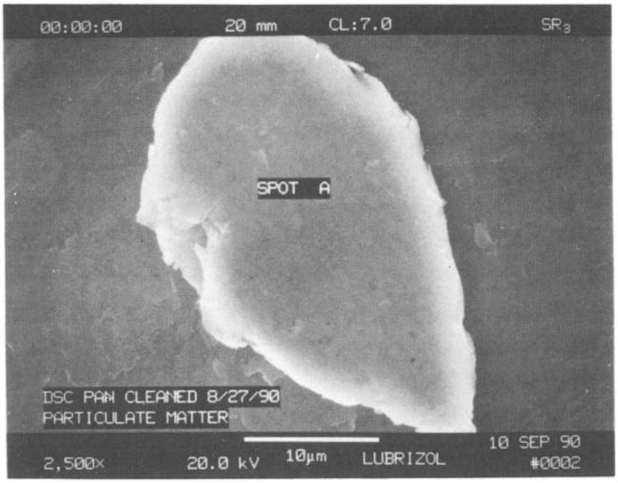

Fig. 11. SEM of large particle (Spot A) in Fig. 10.

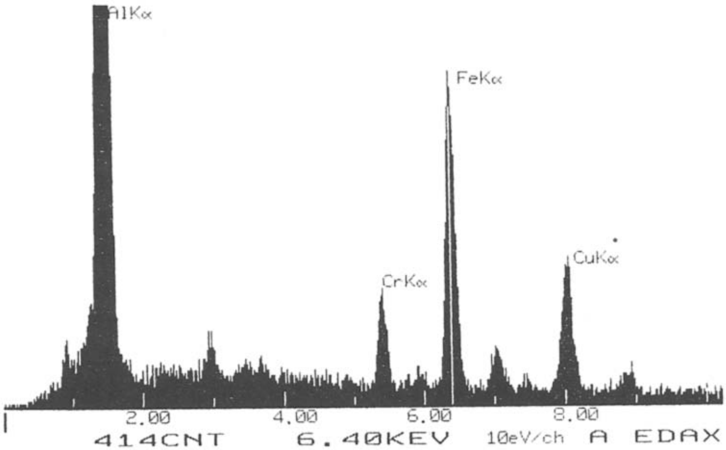

Fig. 12. EDS spectrum of Fig. 10.

TABLE 2

Elemental analysis of pan surface

Al Pan	Fe	Cr	Cu	Fe/Cr
Poor	414	135	173	3.1
Fair	328	103	136	3.2
Good	315	235	157	1.3

TABLE 3

Optimum test conditions for OIT test

Pan type: anodized aluminum (evaluate pan by SEM/EDS)
Temperature: 175°C (isothermal)
Pressure: 500 psig oxygen
Sample size: 100 mg
Gas flow rate: 100 ml min^{-1} (reverse flow)
Heating: ambient to 175°C at 40°C min^{-1}

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