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NOTE

Near Critical Carbon Dioxide Extraction of Oxidation Products from Base Stock Mineral Oils

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Abstract

The use of carbon dioxide at its near critical conditions for the extraction of oxidation products from mineral oils is described. Paraffinic and naphthenic additive-free base stock oils with acid numbers exceeding those specified by the manufacturers were subjected to carbon dioxide extraction. The original specified limit on acidity was achieved using the above technique while retaining the required characteristics of the mineral oils studied. Infrared spectroscopic results confirmed the effectiveness of the removal of the oxidation products by the above technique.

INTRODUCTION

The degradation of mineral oils composed mainly of paraffins, cycloparaffins (naphthenes), and aromatic compounds by atmospheric oxidation during long periods of storage and on agitation upon transportation can lead to the development of oxidation products and insoluble resinous matter, all of which impair the quality of the oil (*1*).

The oxidation products are composed mainly of carboxylic and hydroxy carboxylic acids (*2*).

In order to achieve the initial conditions of the mineral oils, many methods have been described for their purification and the removal of oxidation products. These include chemical treatments such as acid treatment, percolation through or contacting with an adsorbent such as clay or alumina, and hydrofinishing (*3, 4*).

It is well known that gases at elevated pressures and particularly at their near critical temperatures become liquid solvents, with an increase in their vaporizing and selective extraction power on the solute depending on the type of gas being used (*5, 6*).

The physical and thermodynamic behavior of compressed pure carbon dioxide near its critical temperature and above critical pressure has been utilized recently for the selective extraction of compounds from complex and heavy organic mixtures (*7–9*).

In this paper we describe the use of carbon dioxide at its near critical conditions for the extraction of oxidation products from mineral oils.

EXPERIMENTAL

The modified apparatus shown in Fig. 1, which is similar to that described earlier (*10*), was used for the extraction of the oxidation products from mineral oils. It consists of five sections: (1) equilibrium cell, (2) vapor sampling bomb; (3) air-driven recirculation pump, (4) expansion system, and (5) glass oil contactor.

The equilibrium cell is constructed of stainless steel. It has a capacity of 1 L and is designed to operate at pressures up to about 140 bar and temperatures up to 200°C. The cell has three ports, A, B, and C. Port B is used initially for filling the equipment with the gas. The other two ports (A and C) are used as the inlet and outlet for the recirculating vapor stream. The vapor sampling bomb, made of stainless steel, was supplied by Ruska Co. It was designed for a maximum working pressure of 800 bar at temperatures up to 200°C and has a capacity of 25 cm^3. The high-pressure recirculation pump (driven by compressed air) is used to circulate the solvent fluid through the equilibrium cell and vapor sampling bomb. The pump was produced by Haskel Engineering Supply Co. The expansion system is that part of the apparatus which contains the contents of the vapor sampling bomb. It consists of an expansion vessel of 40 L capacity and two glass mineral oil contactors (Fig. 2), 5 cm in diameter and 10 cm in length. All the piping in the high-pressure part of the apparatus is of stainless steel, 0.635 cm diameter, though plastic tubing is used to connect the manometer to the expansion system. The air bath temperature is controlled by an automatic temperature controller supplied by Parr Instrument Co. The temperature of the extremities of the bath were maintained at ±0.5°C of the required temperature.

Two Heise pressure gauges reading between 0 and 300 bar in increments of 1/2 bar are connected to the recycle line immediately above the equilibrium cell and the vapor sampling bomb, as shown in Fig. 1.

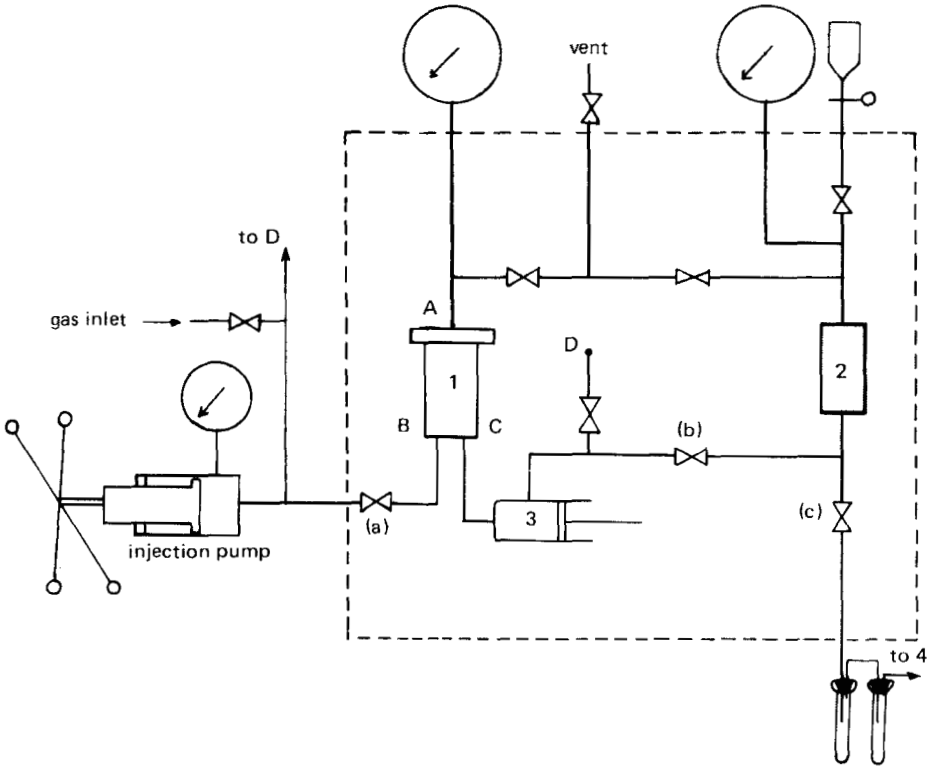

FIG. 1. The apparatus used for the extraction of oxidation products.

The experiment was started by pouring the oil (18 cm^3) into the glass contactor (the contactor was weighed before and after insertion of the oil). After charging the contactor, it was lowered into the equilibrium cell. The equipment was evacuated to remove traces of air, and then charged with carbon dioxide to a suitable pressure via Valve (a) at the required temperature.

The carbon dioxide, at 298.15 K and 85 bar, was allowed to remain in contact with the oil sample for the pumping period (20 min) in order to achieve equilibrium. A slow stream of liquid carbon dioxide was then allowed to enter the recirculation pump via Point D, which is connected to the injection pump, while Valve (b) was closed.

At constant pressure and temperature, the extract (0.3 cm^3) was collected in 0.15 cm^3 increments continuously in the glass receiver by gently opening Valve (c).

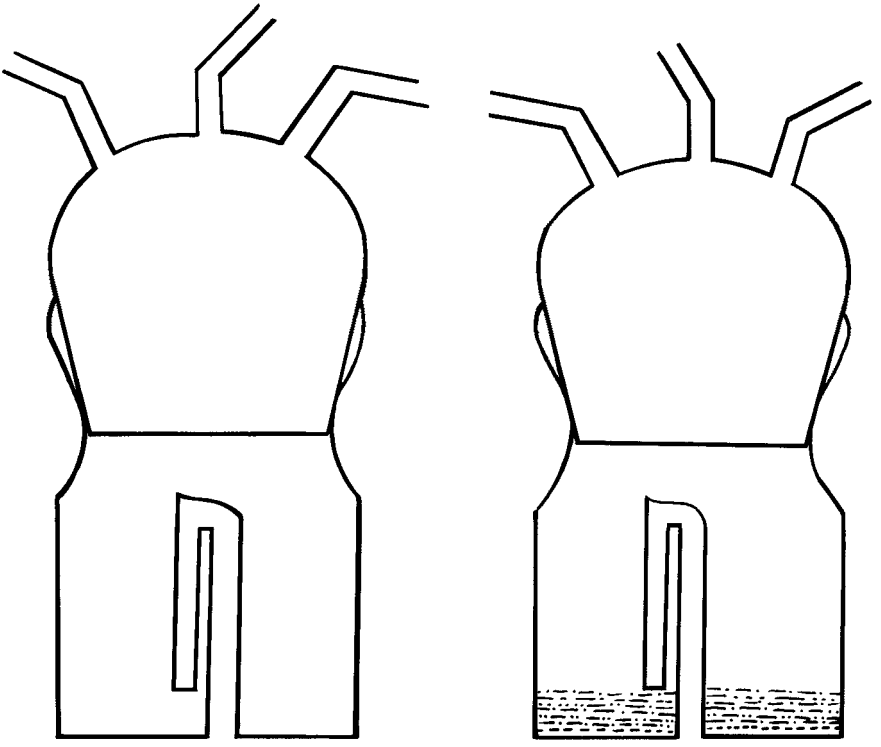

FIG. 2. Glass contactors with and without oil sample.

The extraction processes were carried out in triplicate on each oil sample. The specifications of the additive-free paraffinic and naphthenic base stock mineral oils are given in Table 1.

The infrared spectra were recorded using a Pye Unicam Model SP3-300 infrared spectrphotometer. Oil and extract samples (5 mg) were applied as a thin layer between two KBr disks. The scanning time was 7 min.

The acid number of the oil samples in mg KOH/g of sample was measured according to ASTM Method D-974.

TABLE 1
Specifications of the Additive-Free Fresh Mineral Oils

Characteristics	Units	Paraffinic based	Naphthenic based
Specific gravity at 20°C		0.865	0.850
Kinematic viscosity at 40°C	cSt	14.5	13.0
Acid number	mg KOH/g	0.05	0.05
Flash point	°C	155	90
Pour point	°C	−7	−60
Water content	ppm	10	10
Total aromatics	wt%	2.5	3.9
Total sulfur compounds	wt%	1.0	0.9

RESULTS AND DISCUSSION

The fresh mineral oils were subjected to accelerated atmospheric oxidation by heating them at 90°C in an open beaker with vigorous stirring until their acid number values reached 0.25 mg KOH/g of sample, which are well outside the limit ($\leqslant$0.15) set by the manufacturer. The oils were then subjected to carbon dioxide extraction as described in the Experimental section. The acid number values of the treated paraffinic and naphthenic base mineral oils were 0.055 and 0.06 mg KOH/g of sample, respectively, and were similar to those of their corresponding fresh oils (Table 1). These values are average of measurements obtained from three treated samples for each type of mineral oil, and they show an estimated repeatability limit of within ±5%. The treated oils retained the original characteristics of the fresh oils shown in Table 1.

The results obtained were further confirmed by infrared spectra recorded for the two types of the mineral oils before and after oxidation and after their extraction, as shown in Figs. 3 and 4.

The carbonyl groups of the oxidation products, i.e., carboxy and hydroxy carboxy acids, usually absorb in the 1690–1750 cm^{-1} wavelength region. The IR spectra show that the absorbance of carbonyl groups decreased upon carbon dioxide treatment of the oils that underwent oxidation and was similar to that of the fresh oils. The IR spectra of the extracts, which are mainly composed of oxidation products, show a very strong absorbance in the same wavelength region.

The behavior of carbon dioxide in removing oxidation products can be attributed mainly to the vapor–liquid phenomena whereby a portion of

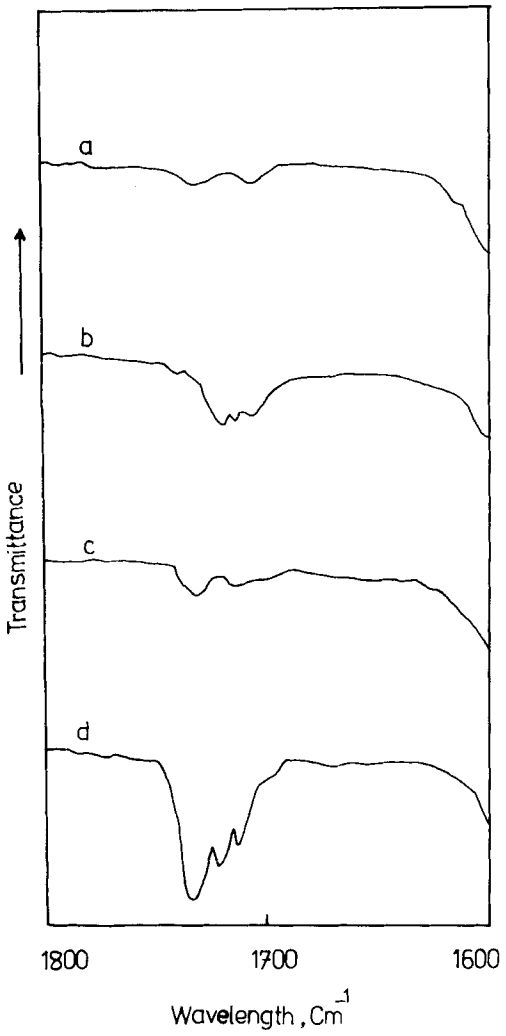

FIG. 3. The infrared spectra of paraffinic-based oil: (a) fresh, (b) oxidized, (c) treated with CO_2, and (d) acid extracts.

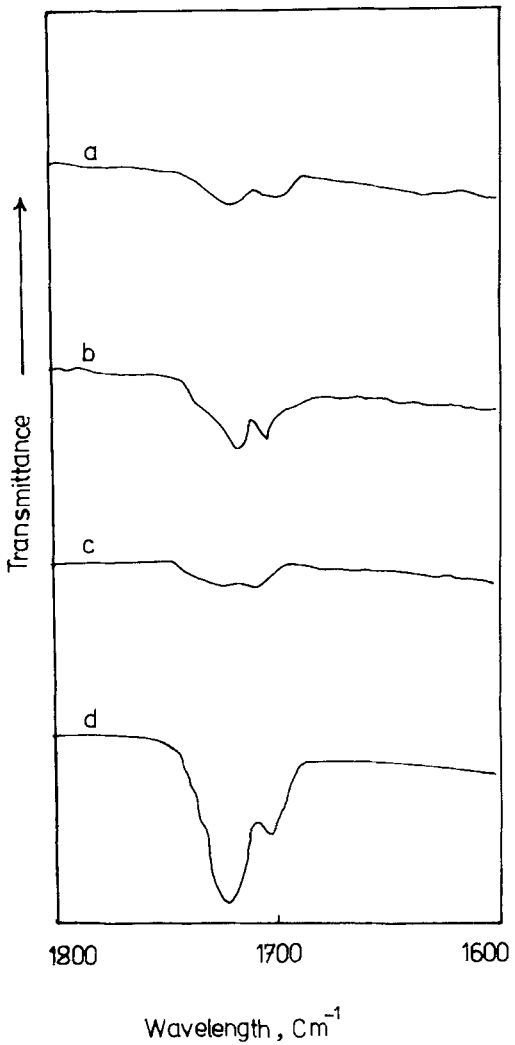

FIG. 4. The infrared spectra of naphthenic-based oil; (a) fresh, (b) oxidized, (c) treated with CO_2, and (d) acid extracts.

the heavy solute (oxidation products) is vaporized in the light solvent phase (carbon dioxide) during repeated recirculation of the light solvent phase through the solute. In addition, the association of solute and solvent can be related to the very slight polarities of carbon dioxide and the oxidation products due to the presence of the carbonyl group which possess an electronegative oxygen atom.

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