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THERMAL AND COLLOIDAL STABILITY BEHAVIOUR OF OVERBASED PETROLEUM SULPHONATE ADDITIVES

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ABSTRACT

The thermogravimetric analysis of petroleum sulphonate additives, the initial decomposition temperature and the maximum rate of gas evolution, as well as the mass loss at 550 ° C, were studied in relation to the degree of the carbonation reaction. It was established that the better the colloidal stability of the additive the higher its thermal stability will be.

INTRODUCTION

Highly basic sulphonates are particularly useful in imparting detergent properties to oils. The high level of alkalinity is achieved through the carbonation reaction, which consists of contacting the neutral detergent with carbon dioxide in the presence of excess metal oxide and promoter.

The loss in the effectiveness of the detergent additives at elevated temperature is directly related to their thermal stability.

By thermogravimetric studies, metal sulphonates have been distinguished by high thermal stability [1–4]. The susceptibility of some synthetic sulphonate additives to oxidation was found to decrease as their colloidal stability increased [5]. No information has been reported on the changes in the thermal stability of overbased petroleum sulphonate additives in relation to the performance of the carbonation reaction. The present work deals with these aspects.

EXPERIMENTAL

The preparation of the additive

Overbased sulphonate additives were synthesised starting with a hydrofinished petroleum base oil. Neutral calcium sulphonate containing 53%

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(m/m) of sulphonate was prepared from the sulphonated oil. A mixture of neutral calcium sulphonate, calcium oxide and hydrocarbon diluent were carbonated with carbon dioxide gas in the presence of methanol as a promoter. Coarse particles and solvents were removed by centrifuging and evaporation.

The percentage of carbon dioxide gas (percentage of the stoichiometric amount in the carbonation reaction) was taken as a measure of the degree of carbonation.

Thermal stability measurements

Thermogravimetric studies were carried out on a Stanton-760 thermal analyser. The measuring conditions were as follows: samples of 3–5 mg were heated up to 550 °C at a rate of 20 °C min^{-1}. An air atmosphere (flow rate, 50 cm^3 min^{-1}) was applied as oxidising medium. The experimental error was within the limit ±3 °C.

The initial decomposition temperature T_i and the temperature at which maximum decomposition rate is observed T_m were used for rating thermal stability of additives. An additional criterion used was the weight loss of the additives upon heating.

Colloidal stability of the dispersions was evaluated by decomposing the additive with 15% (m/m) of distilled water at 110 °C for 4 h and precipitating with benzene followed by centrifuging [5].

The decrease in alkalinity, expressed in percentage of the original, was regarded as the measure of the colloidal stability. The reproducibility of the results was ±2%.

RESULTS AND DISCUSSION

Modification of the ratio of the reactants used in the overbasing reaction gave transparent products with the required total base number. The properties of the additives, which were obtained using a stoichiometric amount of carbon dioxide gas, are listed in Table 1.

The thermal and colloidal stabilities of the additives are described in Table 2. While the colloidal stability of the dispersions remained unchanged, the thermal stability was found to decrease slightly as the level of alkalinity increased.

These data indicate that it is feasible to obtain stable additive dispersions by performing the carbonation reaction in the presence of calcium oxide in an amount corresponding to the required alkalinity.

In order to establish the effect of a decrease in the degree of carbonation on the thermal behaviour of the sulphonates, a product with a desired total alkalinity of 300 mg KOH g^{-1} was prepared under the same conditions used

TABLE 1

Physicochemical properties of the sulphonate additives (stoichiometric amount of carbon dioxide gas)

Property	Alkalinity (mg KOH g^{-1})		
	160	300	430
% Sulphated ash (m/m)	14.5	33.1	43.5
% Content of carbonates (m/m)	12.3	24.7	35.3
% Water content (m/m)	0.01	0.01	0.01

TABLE 2

Stability characteristics of the additives

Stability characteristic	Alkalinity (mg KOH g^{-1})		
	160	300	430
Colloidal stability (%)	84	85	84
T_i (°C)	264	253	251
T_m (°C)	340	332	329
% Weight loss up to 550°C (m/m)	74.1	69.0	61.4

TABLE 3

Change in stability of the sulphonate additive upon reducing the degree of carbonation

Colloidal stability (%)	94
T_i (°C)	271
T_m (°C)	345

in preparing the additive having an alkalinity of 300 mg KOH g^{-1} (which are described in Table 1), except that the degree of carbonation was lowered to 90%. The resulting additive had an alkalinity of 290 mg KOH g^{-1}.

The stability characteristics of this product (Table 3) demonstrate that a simultaneous increase in both thermal and colloidal stability occurred.

In accordance with the data obtained, the decrease in the degree of carbonation, which reduces the content of calcium carbonate in the alkaline component of the additive, improves the colloidal and the thermal properties of the dispersions.

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