Influence of elemental sulfur and mercaptans on corrosion of copper strips in the ASTM D-130 test by means of electronic microscopy (SEM) and energy dispersive X-ray (EDX)

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Summary. Crude petroleum contains sulfur compounds, most of which are removed during refining. The corrosivity of sulfur compounds present in petroleum products is measured by means of the ASTM D-130 copper strip test, which is based on discoloration of a standard copper strip immersed into the petroleum products at 50 °C for 3 h. Here the corrosivity of copper strips are tested with elemental sulfur and different mercaptans in synthetic naphtha. The great corrosive power of elemental sulfur is 3.7 times higher than that of ethylmercaptan, the most corrosive among the different mercaptans. The elemental sulfur and ethylmercaptan corrosion distribution on copper strips is also studied by means of the ASTM D-130 test together with electronic microscopy (SEM) and energy dispersive X-ray (EDX) techniques. These non-destructive techniques allow to know the strip corrosive morphology and to determine the sulfur concentration on the strip.

1 Introduction

The corrosive properties of naphthas are governed by their content of corrosive sulfur compounds, such as elemental sulfur, mercaptans, sulphides, disulphides, etc. [1 - 4]. These may be inherently present in the naphthas or may sometimes get introduced during sweetening treatments [5] using elemental sulfur of mercaptan removal. The corrosive activity on various metals can vary according to the chemical type of sulfur compound present. The copper strip corrosion test is designed to assess the relative degree of corrosivity of a petroleum product; this test consists of placing a copper strip in 30 ml of petroleum naphtha at 50 °C. After 3 h the color of the strip surface is compared visually with the ASTM copper corrosion standards [6].

Copper strip corrosion caused by sulfur compounds in petroleum products generally produces a very thin layer, often only a few tenths μm thick; for this reason it is necessary to use specific methods of surface analysis and micro-analysis methods for determining the sulfur concentration on the copper strip surface. Roffey [7] et al. have developed a method to evaluate the corrosivity of petroleum products using piezoelectric crystals. Holm [8] et al. have published a paper about surface analysis methods for the investigation of corrosion inhibitors, using ESCA, AES, SIMS and LAMMA techniques applied to the system copper/benzotriazole or tolyltriazole in tap water. Schreifels [9] et al. have published a study on copper corrosion inhibition in sour hydrocarbon fuels. Inhibitor film characteristics and corrosion product composition on the copper strips using the ASTM D-130 test are determined by Auger electron spectroscopy (AES). In a previous paper [10] electronic microscopy (SEM) and energy dispersive X-ray (EDX) techniques were used as techniques of great interest in the study and determination of sulfur concentrations on the corroded surface of copper strips. In the present paper the contribution of elemental sulfur and different kinds of mercaptans (linear and cyclic aliphatics and aromatics) in the copper strip corrosion in synthetic naphtha is studied by means of electronic microscopy (SEM) and energy dispersive X-ray (EDX) techniques. Furthermore, the corrosion distribution produced by elemental sulfur and ethylmercaptan on the copper strip surface is studied with the same techniques.

2 Experimental

2.1 Apparatus

A scanning microscope ISI-DS-130, with energy dispersed X-ray (EDX), model Kevex 8000 was used. The intensity of the Kα-lines of the sulfur- and copper-EDX signals are converted to % sulfur by means of the correction formulae [11] ZAF (correction for the effects of atomic number, Z, absorption, A, and fluorescence, F) and MAGIC (microprobe analysis generalized intensity corrections), the
instrument having been previously calibrated [12] with metallic copper and aluminium.

In the previous paper [10] an optimization of the experimental parameters was carried out in order to increase the sensitivity. Surface analyses were carried out at 20 KV, the penetration depth of electron beam was 0.76 μm. The distance between the electron gun and the sample “working distance” was 13 mm. The incidence angle of the electron beam on the sample was 35°. The distance between the detector, Si(Li), and the sample was 20 mm. The counting time was 100 s for all experiments. The area sampled [13] corresponds to one window 75 mm × 75 mm in size, measured on the screen and with the lowest magnification, equivalent to 1.706 mm² of sample. A thermostatic bath was used for the ASTM D-130 test, model GGT (Torino, Italy).

2.2 Chemicals

Crystalline sulfur (PANREAC) was dissolved in synthetic naphtha and used as standard. The synthetic naphtha was 70% petroleum ether (b.p. 65–95°C) and 30% benzene. Ethylmercaptan, propylmercaptan, butylmercaptan, pentylmercaptan, hexylmercaptan, cyclohexylmercaptan, heptylmercaptan, octylmercaptan, thiophenol, p-thiocresol and benzylmercaptan were obtained from Aldrich Chemie.

2.3 Procedure

The copper strips were polished first with 65-μm silicon carbide paper, washed with isooctane and then polished again with 105-μm silicon carbide grains picked up with a cotton pad moistened with isooctane. Rub in the direction of the long axis of the strip. Once the copper strips had been polished and cleaned of any metal dust, they were immersed in 30 ml of the sample and heated at 50°C for 3 h [6]. At the end of this time the copper strip was removed, washed with isooctane and compared with the ASTM copper strip corrosion standards. Then the copper strip was studied by means of EDX under the conditions indicated.

3 Results and discussion

3.1 Matrix hydrocarbon influence on the corrosion produced by elemental sulfur and ethylmercaptan

In order to carry out a systematic study of the corrosion produced by sulfur compounds present in petroleum naphthas, the influence of aliphatic (petroleum ether 65–95°C) and aromatic (benzene) hydrocarbons on the corrosion produced by the elemental sulfur and ethylmercaptan is studied.

Fig. 1 shows the sulfur concentration on the surface of copper strips treated with 5 mg/l of elemental sulfur and 5 mg S/l of ethylmercaptan when the ratio benzene/petroleum ether is varied in the matrix hydrocarbon. The results indicate that for the same elemental sulfur and ethylmercaptan concentration studied, the corrosion produced by elemental sulfur is higher than that of ethylmercaptan corrosion. Moreover, the different compositions of the matrix of hydrocarbons do not affect the corrosion. The ASTM D-130 rating is 4a for elemental sulfur and 1b for ethylmercaptan. The mixture, 70% petroleum ether and 30% benzene, is taken as synthetic naphtha (SN); this composition is similar to commercial naphthas.

3.2 Corrosion studies with mercaptans

Mercaptans together with elemental sulfur are the most common sulfur compounds present in petroleum products. The corrosion produced by linear aliphatic (from ethyl to octylmercaptan), cyclic aliphatic (cyclohexylmercaptan) and aromatic (thiophenol, p-thiocresol, benzylmercaptan) mercaptans is studied in synthetic naphtha.

Figure 2 shows that the corrosion produced by linear mercaptans decreases when the number of carbon atoms increases. The relationship between the sulfur concentration on the copper strips and the number of carbon atoms in linear mercaptans is a decreasing exponential function. Among the linear aliphatic mercaptans studied, only ethylmercaptan and propylmercaptan produces corrosion on copper strip. It is possible that methymercaptan can be more corrosive than ethylmercaptan but its low boiling point makes it impossible to test it.