Various gases are used as protective and reducing media in the radioelectronics industry. When these gases are contaminated, the percentage of rejected parts manufactured in a given plant will increase sharply [1]. A special danger is presented here by vapors and aerosols of oil that unavoidably gets into the gases during compressor operation [2]. Since processing operations in these gas media are conducted at temperatures as high as 600°C, the oil is subjected to the action of such temperatures. In order to resolve certain problems of production technology improvement and process gas purification, information must be available on the state of the oil in the gas, conversion of the oil on the surfaces of the articles, the action of the medium on the oil, and other factors.

In this article we are discussing the solution of a narrow and specific group of problems related to the determination of the state of oil when it is heated, and we are also proposing a method of studying mineral oils that can be used successfully in the petroleum refining industry.

In our studies, we have used a derivatographic method that combines the following methods of thermal analysis.

1. Differential thermal analysis (DTA) is a method which was proposed long ago by LeChatelier [3]. The principle of DTA measurement has been slightly modified since that time: it now consists of measuring the enthalpy of the test material by means of thermocouples connected in a so-called differential circuit [4, 5].

2. The thermogravimetric (TG) method is based on periodic heating and weighing of the test material. Currently, measurements by this method are made by means of a thermobalance that measures and continuously records the sample weight change.

3. Derivative thermogravimetry (DTG) is of independent value, and it also supplements to a considerable degree the thermogravimetric method by recording the differential curve of weight loss or gain of the test material.

All of these methods are ordinarily used separately. However, the entire combination of complex thermal analysis can be carried out simultaneously on a single sample by means of an apparatus known as a derivatograph of the system of Paulik, Paulik, and Erday.

Such analysis is carried out with small samples, which give more accurate results [6-10] and a clearer manifestation of thermal effects arising in the process of chemical and physical conversions. Weight loss and rate of weight loss can be calculated from the TG and DTG curves. The DTA curves make it possible to determine the energy consumption related to conversion of the test material, or the amount of energy evolved in the process of heating.

The TG, DTG, and DTA curves, along with the temperature curve (T), are recorded automatically on photographic paper; such recordings may be made at various levels of sensitivity.

The oil test sample is placed in a platinum crucible in the furnace of the instrument. The sample is weighed on a thermobalance set for maximum sensitivity (0.2 mg). The sample weight is chosen with regard for a number of factors. When a small quantity of oil is present, the test is run with the smallest crucible. The amount of sample should be such that the tapered part of the crucible is filled, but the oil does not overflow when heated. The sample size should be adjusted to the heating rate and the magnitude of the postulated changes in heat content.
Figure 1 is the derivatogram of an oil taken over a temperature range of 20 to 300 °C in a stream of air. The conditions of the experiment (as stated in Fig. 1) signify that the DTA curve was recorded at maximum sensitivity, the DTG curve was recorded with 1/5 maximum sensitivity, the full-scale weight loss was 50 mg (0.5 mg per division), and the maximum temperature of the experiment (300 °C) was reached in τ = 400 min. The weight of the KS-19 oil sample was 544 mg.

A general inspection of the derivatogram shows that heating caused the oil sample weight to decrease, at first slowly and then sharply. Here the process of weight decrease (TG curve) was accompanied at first by energy consumption (downward trend of DTA curve) and then by energy evolution (upturn of DTA curve). A more detailed examination of the curves makes it possible to distinguish the temperature intervals in which oil conversions occur and, to some degree, to interpret them.

The course of the TG curve in the interval 42-205 °C indicates a proportional decrease in oil weight with time (section A-B) owing to oil evaporation. The rate of weight loss was also constant: the DTG curve (A-B) is linear. It has been established by chromatography that the volatile fraction of the KS-19 oil includes 16 hydrocarbons from C₅ to C₈.

As would be expected, energy was consumed in evaporation, in amount proportional to the area A'B'C'D'A' of the endothermic peak of the DTA curve. By means of calibrated derivatograms, it is feasible to determine the amount of energy consumption in evaporation. Thus, the area A'B'C'D'A' corresponds to a consumption of about 85 cal, or 3.4 kcal/g based on the weight loss.

The endothermic effect (point C) reached a maximum at 240 °C. The weight loss at this moment was 12.5 mg (2.3% of sample weight). A turbine oil conforming to GOST 3253, when heated to 240 °C under analogous conditions, was 40% evaporated. Thus, the volatility of the KS-19 oil is low. We obtained analogous results in determinations of the volatility of compressor and turbine oils by a procedure proposed by VNII NP [11].

An examination of the state of the oil between 205 and 240 °C is of particular interest. Here the rate of sample weight decrease became appreciably greater: the section B-C of the DTG curve was steeper, and the absolute magnitude of the weight loss was greater than in the 42-205 °C range. It would seem that the sharp weight loss should correspond to a sharp decrease in the DTA curve, which indicates energy consumption. However, the DTA curve not only did not turn sharply downward, but on the contrary began to rise at the point C', indicating energy evolution. Thus, within this temperature range, along with energy consumption in oil evaporation, conversions took place in the oil: these are related to the energy evolution. We relate these conversions to oxidation of the oil hydrocarbons by atmospheric oxygen, since the heating was performed in an air medium. Up to 240 °C, the amount of energy absorbed by evaporation at higher temperatures, the evolved energy was considerably more than that absorbed.

* Subsequently (in the figures) the experimental conditions are written in abbreviated form.
† In subsequent use, the word "section" is omitted from the letter designations.