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SENSITIVE DETECTOR OF EXOTHERMIC PROCESSES (SEDEX)

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ABSTRACT

Sedex is a new apparatus to detect the initial temperature of exothermic processes in substances and reaction mixtures under industrial operating conditions. It is based on a slow heating of samples in a special oven, the detection of any difference between the oven and sample temperatures and the evaluation of this difference. The features and advantages of this method are indicated. The properties of this instrument make it especially useful for industrial applications or anywhere where large numbers of samples must be checked for exothermic processes. Additionally, Sedex provides information about the endothermic changes which may occur in the sample.

INTRODUCTION

When carrying out chemical reactions, one of the most important items of information about a substance or a reaction mixture is a knowledge of the existence of any reactions or processes with heat effects. From the standpoint of safety, exothermic reactions are the most important of these and the decisive characteristic of an exothermic process is its initial temperature.

A considerable number of measuring methods and devices for determining the initial temperature of exothermic processes are now available, such as DSC, DTA, TG, the so-called dynamic decomposition test (Kühner—Geigy test), Sikarex (an adiabatic calorimeter developed by Sandoz), etc. The following features are expected of a device for determining the initial temperature of exothermic processes in the chemical industry.

(a) High sensitivity.

(b) A mode of operation conformable to plant conditions, e.g. simple stirring of test samples; investigations of samples under any desired (inert) gas, or while bubbling gas through the sample; and the possibility of using any desired sample container.

(c) Economy, e.g. low price of the apparatus; simultaneous measurement of several samples (high productivity); and prompt and reliable results.

(d) Simplicity, e.g. simple in function and easy to operate; and simple and objective interpretation of the results.

Unfortunately, none of the devices presently on the market fulfils these expectations. This accordingly gave the impetus to develop a new sensitive detector of exothermic processes (Sedex).

PRINCIPLE

The sample is heated up in a suitable receptacle (e.g. a 50 ml glass beaker) by means of a gaseous medium whose temperature rises in linear fashion. The temperatures of the heating medium and of the sample are measured by means of suitable sensors (preferably Pt-100 sensors) and registered on a recorder having at least 3 channels. At the same time, the difference between these temperatures is generated and registered with a much (normally 10 times) greater sensitivity on the same recording device. If there is no process with heat effect taking place in the sample, the difference between these two temperatures remains constant. The temperature at which the difference begins to decrease is the initial temperature of an exothermic process. Conversely, the temperature at which the difference begins to increase is the initial temperature of an endothermic process.

DESCRIPTION

The Sedex is essentially composed of 4 parts (Fig. 1), (a) a chamber which can be heated with circulating gas, sample holders and stirrer (oven), (b) a controlling device to give a linear rise in temperature, (c) temperature sensors, and (d) a recorder.

Oven

One of the most important prerequisites of an oven that is suitable for the intended purpose is a homogeneous spatial distribution of temperature within its working area. In the Sedex, this is assured by a system consisting

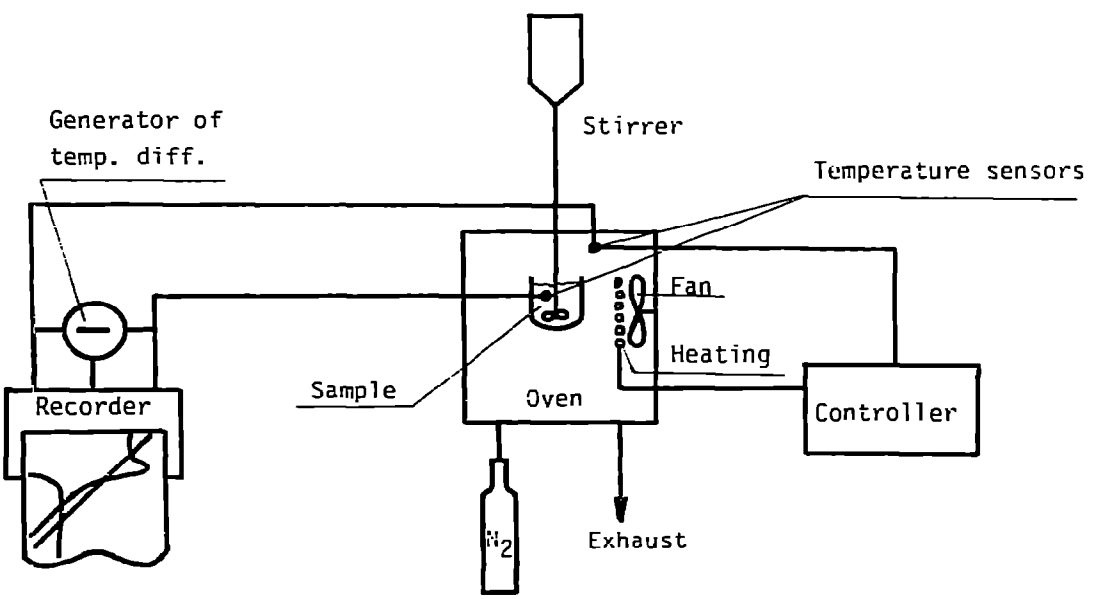

Fig. 1. Schematic diagram of Sedex.

of a heating coil and a fan. The electric output of the coil is 300 W. The oven housing is constructed of stainless steel with asbestos insulation. Inside the oven is the sample holder. This consists of a steel rod 1 cm in diameter which is fixed to a removable tray of sheet steel and to which are attached two laboratory clamps. This permits two sample containers to be held and two samples to be investigated simultaneously. The sample containers are normally beakers of 50 ml capacity, but it is quite possible to use other containers if this should prove necessary or desirable. A sulphonating flask and an autoclave have been successfully tested for this purpose. In most cases, however, glass beakers are adequate. The removable tray under the samples prevents liquids or molten substances from getting into the interior of apparatus and permits easy cleaning.

The measurements can be carried out either in air or under any desired gaseous atmosphere. This is particularly advantageous when there is a presumption that oxidation of the test substance with atmospheric oxygen could take place before the actual initial temperature of the expected exothermic process is reached. Inert conditions are best achieved by using nitrogen. For this purpose, the oven is fitted with two nipples, one serving to introduce the gas and the other for connecting the exhaust pipe. A flow rate of 50 l h^{-1} assures an adequate elimination of atmospheric oxygen (oxygen residue approx. 1 vol. %) without disturbing the uniform distribution of temperature within the oven. In the upper wall of the oven there are openings for the temperature sensors and for the stirrer shaft (Sovirel system). Stirring is not necessary in every case, but it is especially recommmended when suspensions are being investigated. It is carried out by a normal glass stirrer driven by a laboratory motor of the usual type with variable r.p.m. settings. In most cases a stirring speed of 100—500 r.p.m. is fully adequate.

Controller

To control the linear rise in temperature a combination of three standard devices from Systag is used.

(a) The Gradient Master Set (Combilab 1250) serves to control the rate of temperature rise. This device permits the heating rate to be set continuously from 1 to 10 000°C h^{-1}. The Sedex system uses a standard rate of 30°C h^{-1} (0.5°C min^{-1}). This heating rate has proved successful; however, in certain cases it is conceivable that it may be either increased or decreased. A slower heating rate is especially advisable with larger samples (>100 ml).

(b) The Pt-100 Converter (Combilab 1242) serves to convert the signal of a Pt-100 sensor into an electric impulse.

(c) The type 1 Controller (Combilab 1241) is the actual proportional controller. At a suitable setting, it assures a perfect linear rise in temperature in the range of 20—400°C.

Temperature sensors

Normal commercial Pt-100 sensors are used for measuring the temperature. In order to generate a suitable signal for the recorder, these sensors are

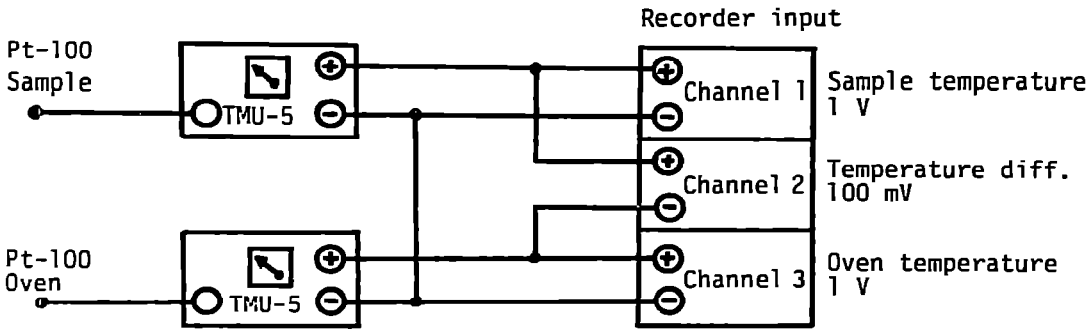

Fig. 2. Schematic diagram of temperature sensing system.

connected to TMU-5 temperature compensators (Systag). The temperature difference is generated by a suitable wiring of the outlets of these measuring compensators (Fig. 2).

Recorder

A recorder with a minimum of three channels is necessary to register the sample temperature, the oven temperature, and the difference between

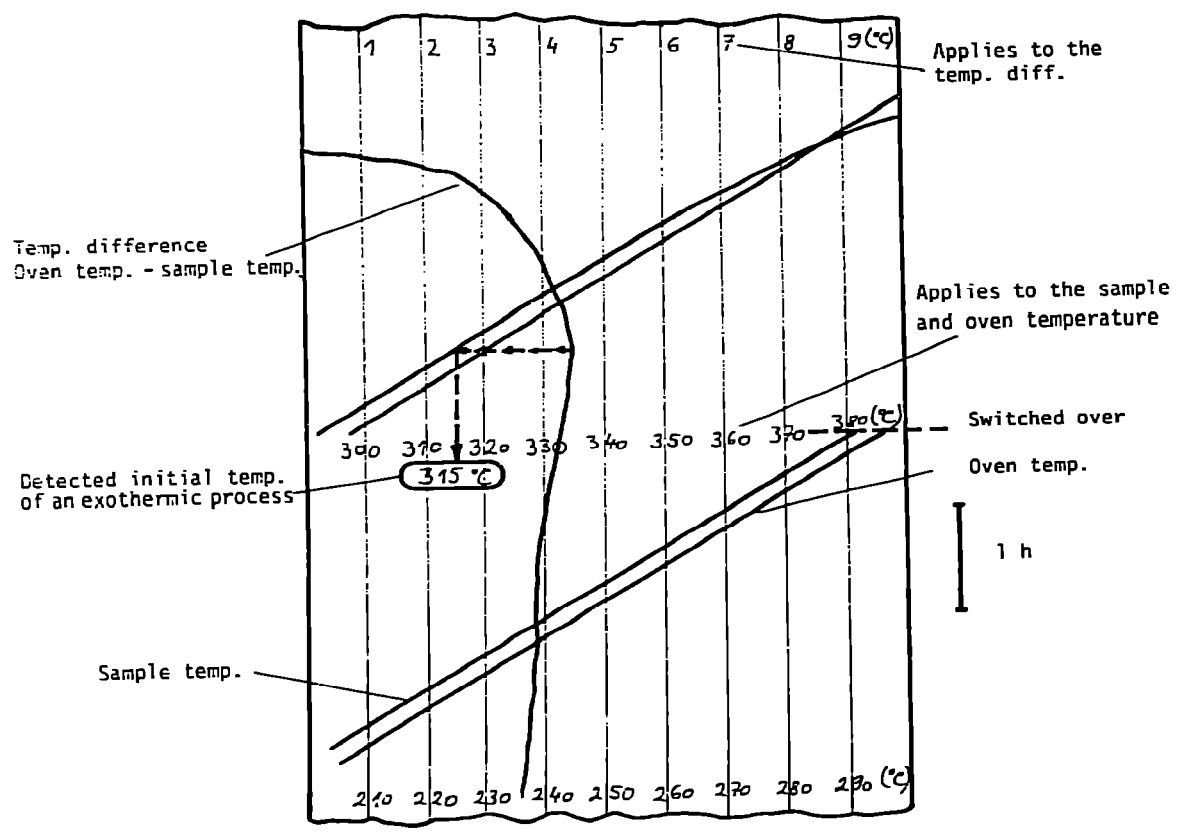

Fig. 3. Evaluation of the thermal stability of 1.5-dinitroanthraquinone.

them. To assure trouble-free evaluation of the measurements, it is advantageous to use a point recorder. The range of 1 V is used for recording the sample and oven temperatures. This means that the full scale on the recorder is 100°C (Fig. 2, channels 1 and 3). For registering the difference in temperature, however, a range of 100 mV is used (see also Fig. 2, channel 2). This means that the full scale for registering the temperature difference is 10°C. This arrangement, in combination with a recording paper speed of 20 mm h^{-1}, permits the reliable detection of a change in the temperature difference of 1°C h^{-1}, which with a sample size of about 30 g corresponds to a detection sensitivity of 0.5 W kg^{-1}. In most cases, this arrangement has been shown to be the most favourable one. However, other combinations of sensitivity and recording paper speed are, of course, quite possible.

EVALUATION

The evaluation is obtained in graphic form directly on the chart paper; it is extremely simple and illustrative (see Fig. 3).

A point recorder is preferred to a pen recorder as the time lag of the signals with a pen recorder makes the evaluation more difficult.

ADVANTAGES

The Sedex apparatus offers the following advantages over other devices for determining the initial temperature of exothermic reactions.

(a) High sensitivity of <1 W (kg sample)$^{-1}$.

(b) Stirrability. The sample can be stirred by a normal laboratory stirrer.

(c) Measurement under a protective atmosphere. The measurements under a protective gas are very simple.

TABLE 1

Comparison of Sedex with other methods

Substance	Initial temperature of the exothermic process (°C)			
	Dynamic decomposition test	DSC	Sikarex	Sedex
p-Xylyl chloride + 0.02% Fe	110	80	80	55
1,5-Dinitroanthrquione	[a]	>370	330	320
Mixture of 1,5 and 1,8-Dinitroanthraquinone	340	330	285	290
1-Nitroanthaquinone	360	[a]	325	295
1-Nitroanthaquinone, raw material	370	380	305	295
Dodecylnitrite	[a]	145	116	115
2,4-Dinitroaniline	310	[a]	[a]	250
p-Nitroaniline	[a]	[a]	273	272

[a] Not measured

(d) Flexibility. Any suitable container can be used for holding the sample (e.g. even an autoclave).

(e) Low price. The complete apparatus, including recorder, costs about SFr. 20 000.

(f) Efficiency. Two samples can be measured simultaneously (this number could easily be extended to 5).

(g) Rapidity. One complete measurement takes 2—8 h.

(h) Simplicity. No special training is required to operate the device; it does not have to be corrected or adjusted during use.

(i) Evaluation. Simple and objective.

(j) Precision and reliability. The measured values agree with the results of methods that are considerably more elaborate in terms of time, price and labour intensiveness) (see Table 1).