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THERMOANALYTICAL INVESTIGATIONS ON DECONTAMINATING AGENTS FOR USE IN NUCLEAR PLANTS

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ABSTRACT

To perform technical routine decontamination work regarding surfaces, apparatus, clothing and employees, specific effective decontaminating agents have been developed. This has been done especially in view of trouble-free working of plants for the treatment of radioactive waste water. One of the main criteria of the applied product is sufficient thermal stability up to 300°C avoiding foam-formation and steam volatility which is demonstrated by the application of the detergents discussed in this paper. In routine decontamination work these products have proven very successful.

INTRODUCTION

To ensure trouble-free working of plants for waste water treatment related to the above questions, the radioactive waste water requiring treatment must be amenable to the normally practised methods of waste water processing.

As a rule the purification of radioactive waste water is carried out by evaporation, filtering and centrifuging. The purified water is collected and, after testing, added to the receiving water. The radioactive concentrates and residues obtained are dressed by incorporating them into matrix materials, like cement or bitumen, or roll-mill dried. After this procedure they are in a suitable form for interim or final storage.

Due to these facts, the properties of decontaminating agents, especially with regard to the applied thermal treatment, are of great importance. Other essential criteria are their behaviour with regard to foaming [1] and steam volatility.

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EXPERIMENTAL

The thermoanalytical investigations were performed by applying constant instrumental settings in a quasistatic air atmosphere, to obtain reliable and comparable results. The heating rate was 5°C min^{-1} and the DTA measuring range 0.05 mV. The TG (DTG) data were recorded in a measuring range of 0.25 mg (0.1 mV) using a Netzsch STA 429 thermal analyser. For a detailed description and applications, see refs. 2–7.

The commercially available decontaminating agents and additive compounds used were HAKA-DEKOPUR RS, HAKA-DEKOPUR W 10 and DEKODUSCH, as well as critic acid, tetra-potassium pyrophosphate and fatty acid triethanolamine salt [8,9]. The sample mass ranged from 30 to 150 mg. The crucible material was alumina and the reference an empty alumina crucible.

RESULTS AND DISCUSSION

The applicability of decontaminating agents in the control area is limited and the requirements which have to be met are listed below:

— no foam formation by the application of primarily low-foaming surfactants
— minimization of steam volatility by avoiding solvents and strongly hydrophobic materials
— no water-insoluble, or partially water-soluble compounds
— no water-insoluble cellulose ether or organic polymers
— no organosilicon compounds
— no halogens or halides
— no ammonia compounds
— no filling materials like sodium sulfate, carbonate or silicate
— no nitrate or nitrite compounds
— no sublimating compounds
— thermal stability up to 300°C

The objective of this report is to describe the thermal stability of decontaminating agents. On thermal treatment of the concentrates, i.e. roll mill drying or incorporation of the residues into cement or bitumen, significant exothermic reaction of the decontaminating agent is undesirable.

Thermoanalytical methods are well suited to the study of reaction pathways, accompanied by thermal effects (DTA) and a mass loss (TG, DTG). The results of the TA experiments are discussed for the examples of three raw material components and three detergent products.

The thermoanalytical curves (TG, DTG, DTA) of citric acid dihydrate are shown in Fig. 1. The decomposition of citric acid occurs in the temperature range 65–310°C with maximum reaction rates at 98, 147 and 230°C. The

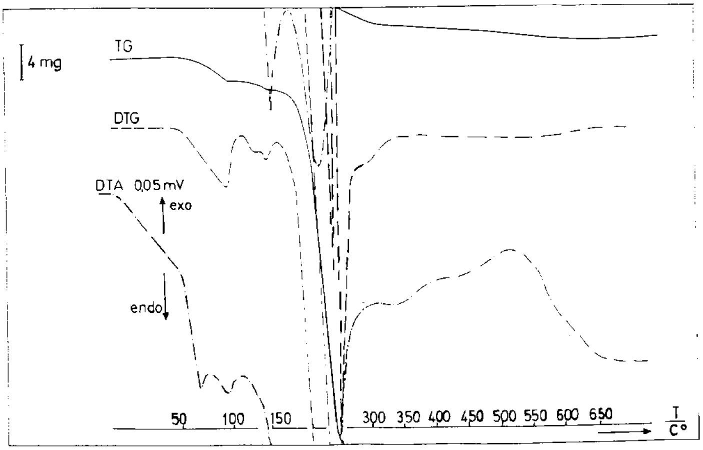

Fig. 1. TA curves of citric acid dihydrate.

endothermic DTA peak temperatures have been estimated at 65, 98 and 221°C. The mass loss data are listed in Table 1.

The TA experiment of tetra-potassium pyrophosphate was carried out to a final temperature of 500°C as illustrated in Fig. 2. The mass loss at 105°C is caused by the loss of water corresponding to an endothermic peak in the DTA curve. The endothermic peak at 263°C is due to the melting of the compound.

The example in Fig. 3 represents the TA curves of fatty acid triethanolamine salt where the temperature ranges up to 627°C with maximum reaction rates at 370 and 425°C. These are accompanied by a first mass loss of 83.7% and a second of 14.9% (total 98.8%) in the temperature intervals 130–400 and 400–570°C, respectively. The DTA peak temperatures are given in Table 2.

The decontaminating agents HAKA-DEKOPUR RS, HAKA-DEKOPUR W 10 and DEKODUSCH are mixtures of surfactants and complexing agents containing citric acid, tetra-potassium pyrophosphate and triethanolamine salt.

In Fig. 4 the TA curves of the decontaminating agent HAKA-DEKOPUR RS, which is used for floors, walls, tools and equipments, demonstrates thermal degradation up to a final temperature of 450°C. No exothermic

TABLE 1

Mass loss data of citric acid dihydrate

Mass loss	Δm_1	Δm_2	Δm_3	Δm_{tot}
(%)	6.9	1.6	87.0	95.5
Temp. range (°C)	65–98	98–188	188–310	65–310

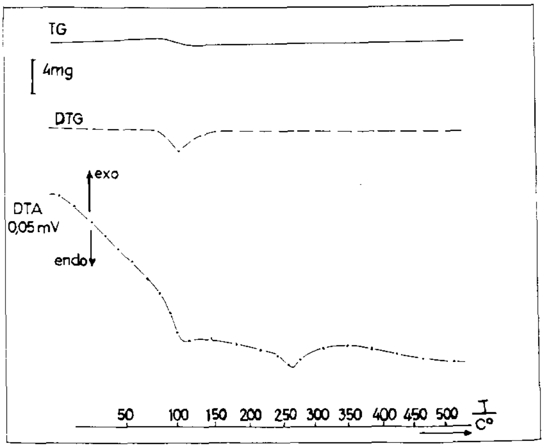

Fig. 2. TA curves of tetra-potassium pyrophosphate.

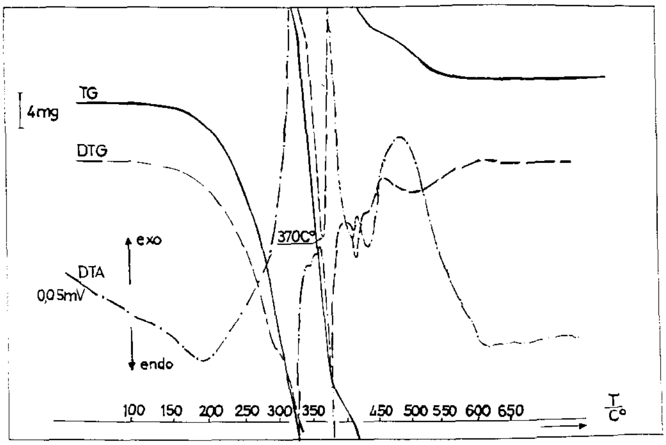

Fig. 3. TA curves of fatty acid triethanolamine salt.

effects in the DTA curve have been detected. The decomposition reaction occurs in a two-stage mass loss. The first in the range 95–118°C with 62.2% mass loss, the second 192–225°C with 16.3% mass loss, giving a total of 78.5%. The maximum ration rates have been estimated at 115 and 203°C corresponding to endothermic DTA peaks at 115 and 200°C, respectively.

TABLE 2

DTA data for fatty acid triethanolamine salt

DTA peak	endo	exo	exo	exo
Temp. (°C)	185	365	420	490

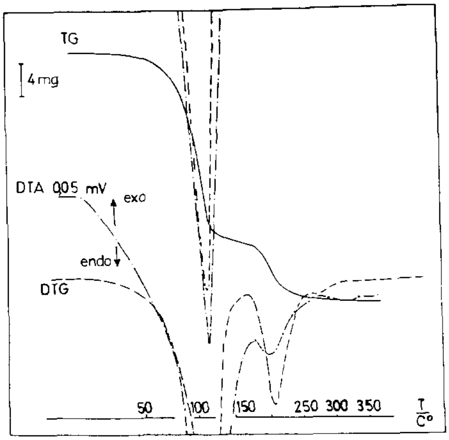

Fig. 4. TA curves of HAKA-DEKOPUR RS.

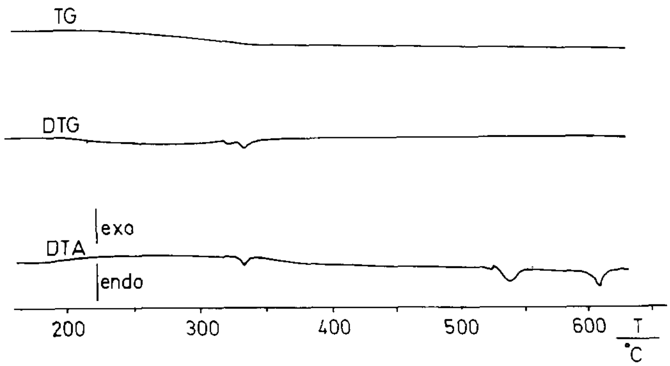

Fig. 5. TA curves of HAKA-DEKOPUR W 10.

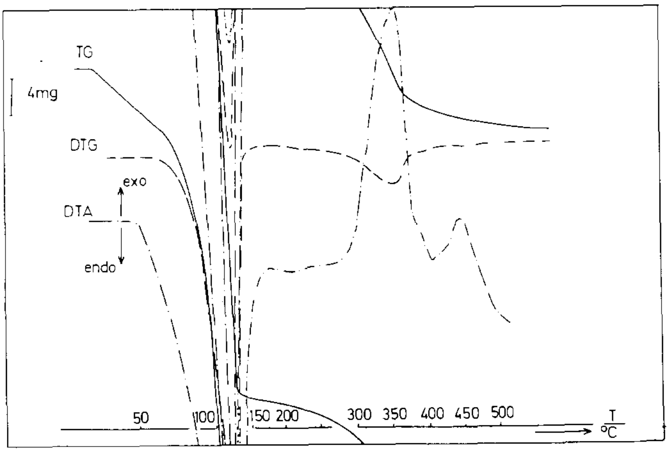

Fig. 6. TA curves of DEKODUSCH.

Another example of thermal stability is the decontaminating detergent for clothes, HAKA-DEKOPUR W 10 (see Fig. 5). The mass loss data have been estimated as 4.7 and 2.3% ranging from 230 to 367°C and from 367 to 650°C, respectively, accompanied by three endothermic peaks in the DTA curve at 334, 537 and 607°C.

As a decontaminating agent for the personnel, DEKODUSCH is used with good results (see Fig. 6). The thermoanalytical investigations were carried out in the temperature range 25–720°C. Mass losses were estimated at 60–115 and 125–370°C with 80 and 16.4% mass loss, respectively. The maximum decomposition rates were estimated at 120 and 370°C. They correspond to two endothermic peaks in the DTA curve at 120 and 378°C, respectively.

By summarizing the results of the TA experiments of the decontaminating agents described in this paper it can be concluded that these products are well suited to decontamination and the results are in good agreement with the requirements mentioned earlier.

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