Gas chromatographic–mass spectrometric separation, identification and determination of C_6–C_{12} cyclic imides in thermally treated epoxy and alkyd resins to locate hot spots inside large electricity generators

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Abstract

A simple and rapid GC–MS method for separation, identification and quantitative determination of long-chain cyclic imides in the 300°C thermally treated epoxy and alkyd resins has been developed. The method provides a positive means of identifying C_6–C_{12} cyclic imide derivatives by GC–MS and enables the specific area of overheating to be identified, thereby averting catastrophic failures of power generators in service. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermal evaporation; Hot spots; Cyclic imides; Imides

1. Introduction

Large electricity generators play an important role in the power distribution system. They are used as a vital component in the generation of power. The reliability of this equipment determines the overall efficiency of the power supply system which is critical in ensuring an uninterrupted power supply to the customer. Any breakdown in these systems causes immense hardships to public life. Generally, such failures are attributed to thermal and oxidative degradation of cellulosic and polymeric material used as insulation [1,2]. The life of these machines is generally based on the standard reference temperature which is set around 40°C. When a hot spot is developed within the generator, the insulating ma-

terial of the windings and other components of the generator are subjected to accelerated aging and its life is reduced. A number of organic materials such as epoxy resin, alkyd resin, nylon paper, phenolic resin impregnated wood, kraft paper, asphalt and lignin sulfonate-based varnishes are used as insulators [3,4]. Hydrogen is used as a coolant not only to keep the temperature below certain limits but also to ensure that no excessive hot spots occur at the windings and other components of the generator [5]. However, in most of the power stations, the demand for power fluctuates over periods of time and the generators are operated to the maximum of their capacity. As a result of this, the insulations are subjected to high temperatures and voltages to meet demands for more energy. At higher temperatures and voltages the insulations undergo rapid chemical changes and their mechanical and dielectrical stabili-

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ty is affected. Electrical faults such as short circuits, loss of cooling, overloads and over voltages lead to the decomposition of insulating materials forming a wide range of degradation products [6–8].

Early work to analyse insulating degradation products has shown that only methane, ethane and ethylene were normally present at levels which were above the detection limits [9]. These results have indicated that most of the degradation products could not be determined without a concentration technique. A number of concentration techniques have been reported in the literature [10–12]. The pre-column technique in which the gaseous products are de-sorbed and flushed on to a gas-chromatograph for analysis was found to be quite useful for estimation of relative amounts of the degradation products of various insulating materials [13]. It is of great value in assessing their potential as characteristic markers. Products resulting from pyrolysis of various types of epoxy resins have been reported in the literature [14]. Bishop and Smith have studied degradation pathways of different insulating materials and ex-plained the source of the products formed [15]. Iglauer has reported that benzene, toluene and aniline were formed from the pyrolysis of nylon paper at 1000°C [16]. Aromatic hydrocarbons and phenols were found to be typical products of degradation of phenolic resins at 700°C [17]. Jackson and Conley have studied the oxidative degradation of phenolic resins and shown that the types of degradation products do not vary over a wide range of tempera-tures [18]. Goos and Reiter have shown that oxygen containing compounds such as alcohols, acids, alde-hydes, ketones, esters and furanes are typical of wood degradation [19]. Wodley has analysed the pyrolysed products of α-cellulose and reported car-bonyl compounds together with alcohols and furanes [20]. All these studies indicate that certain groups of compounds resulting from the degradation of a particular insulating material may be picked out as markers. However, in practice it was found to be quite difficult due to lack of reliable techniques for their identification and quantification. Several reports have appeared in the literature describing the dif-ficulties involved in interpreting the results obtained by GLC. The reliability of this technique has been questioned very often because of the interference of the background level of gases that are generally

present in aged generators [21]. On-line monitoring of the gaseous products has been attempted, but it has not been successful for detecting the faults at early stages [22]. Therefore, the development of alternative techniques is important for the early detection of failures of generators in service.

The latest developments in monitoring the per-formance of electricity generators have indicated the possibility of locating an emerging fault by liberation of certain chemicals applied through paints on the vulnerable areas inside the generator [23]. Our laboratory has recently evaluated a few of such commercially available chemicals and paints iden-tified as generator tagging compounds. These are thermally stable C_6–C_{12} cyclic imide derivatives applied to critical areas of the generator, enabling the specific location of over heating to be identified. These materials provide a positive means of identify-ing C_6–C_{12} in hydrogen cooled generators equipped with a generator condition monitor. A sample of overheated imide is collected and analysed for locating the hot spot zone and thereby averting catastrophic failures in generators.

The present paper describes a simple, rapid and reliable analytical method for separation and identifi-cation of long chain cyclic imides in the thermally treated epoxy and alkyd resins to locate hot spots and monitor the performance and predict the service life of generators in service.

2. Experimental

2.1. Materials and reagents

All reagents used were of analytical-reagent grade unless stated otherwise. Methanol obtained from spectrochem (Bombay, India), IOLAR-grade nitro-gen and helium from BOL (Bombay, India), imides and their formulations provided by M/s BHEL, R&D (Hyderabad, India) were used.

2.2. Apparatus

A gas-chromatograph (Shimadzu, Kyoto, Japan) equipped with an electron-capture detector (ECD) and a fused-silica capillary column DB-17 HT, J&W (30 m×0.32 mm I.D., 0.1 μm film thickness) was

used. Peak retention times and areas were calculated using a microprocessor connected to the instrument. A Micromass 70-70H mass spectrometer coupled with a Pye-Unicam gas chromatograph was used for GC–MS studies. A Pyrochem wilke chamber consisting of temperature control filament and provision for creation of vacuum and cooling was used for heating the imides at elevated temperatures.

2.3. GC-ECD

The six unencapsulated imides were separated on a fused-silica capillary column DB 17 HT (30 m× 0.32 mm I.D., 0.1 μm). The carrier gas was nitrogen, constant flow 0.9 ml/min and the make up gas was nitrogen, constant flow 40 ml/min injection temperature: $T_{inj}=320°C$; detector temperature: $T_{det}=325°C$. The temperature programme was as follows: initial period 100°C for 1 min, then 20°C/min to 300°C held for 2 min.

2.4. GC–MS

Analyses were carried out on a fused-silica capillary column HP-5 (30 m×0.25 mm I.D., 0.25 μm). The carrier gas was helium, constant flow 0.8 ml/min. Splitter (1:20) (period 1 min), 2 μl, injection temperature: $T_{inj}=300°C$, detector temperature: $T_{det}=320°C$. The temperature programme was as follows: initial period 100°C for 1 min, then 20°C/min to 300°C, held for 1 min. Ionization voltage: 70 eV. Transfer line temperature was 280°C. The selected scan range was 1 to 600 u.

2.5. Sample preparation

Solutions containing 1–10 ng/μl of unencapsulated imides in methanol were prepared and 20 μl of each were injected on to the chromatograph. Encapsulated imides consisting of a pigmented chemical powder of an organic dye such as sudan yellow/orange to give different colours to the formulations were mixed with epoxy resin and cured by heating at 140°C for 24 h. During the process of curing the epoxide and the cyclic imide are cross-linked together in the form of a network without changing their physical and chemical identity. About 5 mg of cured formulation containing 0.5–5.0 (% w/w) of

imide was thermally evaporated at a temperature of 300°C for 20 min and then dissolved in 5 ml of methanol and analysed by GC-ECD and GC–MS, successively. Blank epoxy and alkyd resins used as medium of dispersion were also pyrolysed and the products were analysed by GC–MS under similar conditions.

2.6. Analytical procedure

Standards of unencapsulated imides and the thermally treated encapsulated formulations were dissolved in methanol and a 20 μl volume of each sample was injected and chromatographed under the above conditions. Synthetic mixtures and the cured formulations were analysed under identical conditions. The peaks were identified by comparing not only with the retention times of standards but also fragmentation patterns obtained by MS.

3. Results and discussion

Fig. 1 gives the chemical structures of the compounds used in the present investigation. It could be seen from Fig. 1 that all the compounds are the different derivatives of long chain cyclic and non-cyclic imides of tetrachloropthalic acid. These unencapsulated imides are stable enough and do not decompose at the temperatures where hot spots generally start forming inside the generator. Since these molecules function over the service life of a generator and evaporate slowly at a very high temperature of 300°C and above, these are applied to different parts of the generators for easy location of hot spots. Specific areas of the generators to which these chemicals are applied are given in Table 1. These chemicals are liberated whenever a hot spot is developed inside the generator and get collected in the sample collector of an on-line condition monitor. Their identification and quantification at regular intervals may give an indication regarding the electrical and thermal stresses which could result into catastrophic failures of generators in service.

Fig. 2 shows the gas chromatographic separation of the imides using a fused-silica column of 30 m×0.32 mm I.D. and 0.1 μm film thickness. The peaks were identified by injecting individual authen-

1. N-cyclododecyl tetrachloro-
   phthalimide (CDTCP)

2. N-cyclooctyl tetrachloro-
   phthalimide (COTCP)

3. N-cycloheptyl tetrachloro-
   phthalimide (CHTCP)

4. N-dodecyl tetrachloro-
   phthalimide   (DTCP)

5. N,N-dihexyl tetrachloro-
   phthalimic acid (DHTCP)
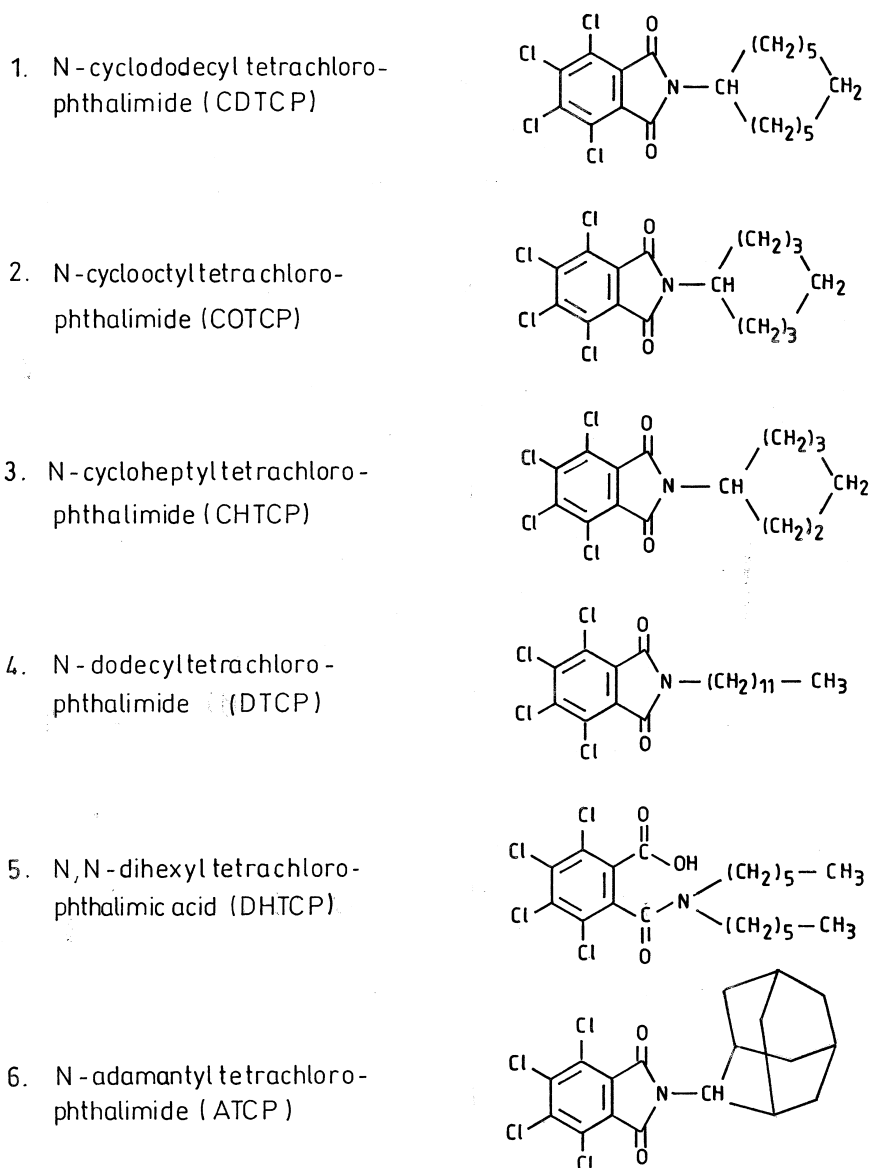
6. N-adamantyl tetrachloro-
   phthalimide (ATCP)

Fig. 1. Chemical structures of (1) CDTCP, (2) COTCP, (3) CHTCP, (4) DTCP, (5) DHTCP and (6) ATCP used as tagging compounds in electricity generators.

Table 1
Cyclic imides and the coating media applied to specific areas of generators

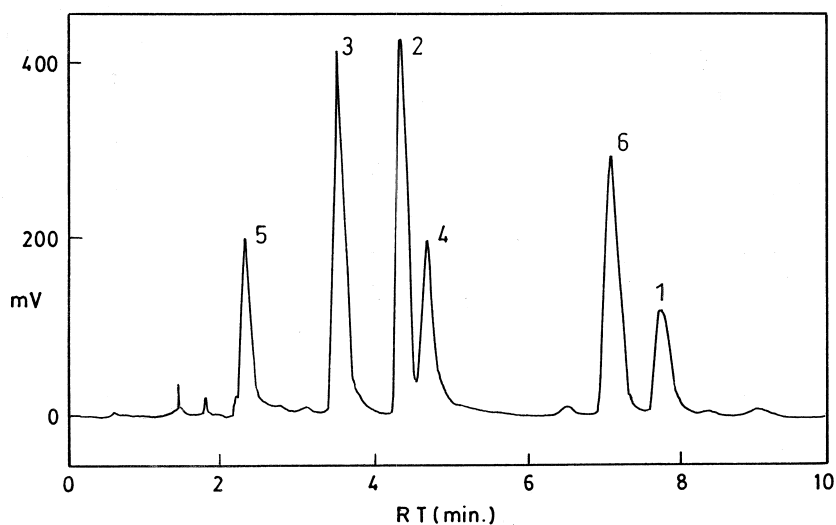| S. No.	Imide	Coating medium	Color	Area applied
1.	CDTCP	Epoxy	Sudan orange	Turbine, end windings
2.	COTCP	Epoxy	Sudan irisol	Core I.D.
3.	CHTCP	Epoxy	Sudan blue	Reactors
4.	DTCP	Epoxy	Sudan yellow	Collector end
5.	DHTCP	Alkyd	Iron blue	Rotor surfaces
6.	ATCP	Epoxy	Green	Bushings and lower leads

Fig. 2. GLC chromatogram of a synthetic mixture of the six cyclic imides used in the present study. For identification and conditions see Fig. 1 and text, respectively.
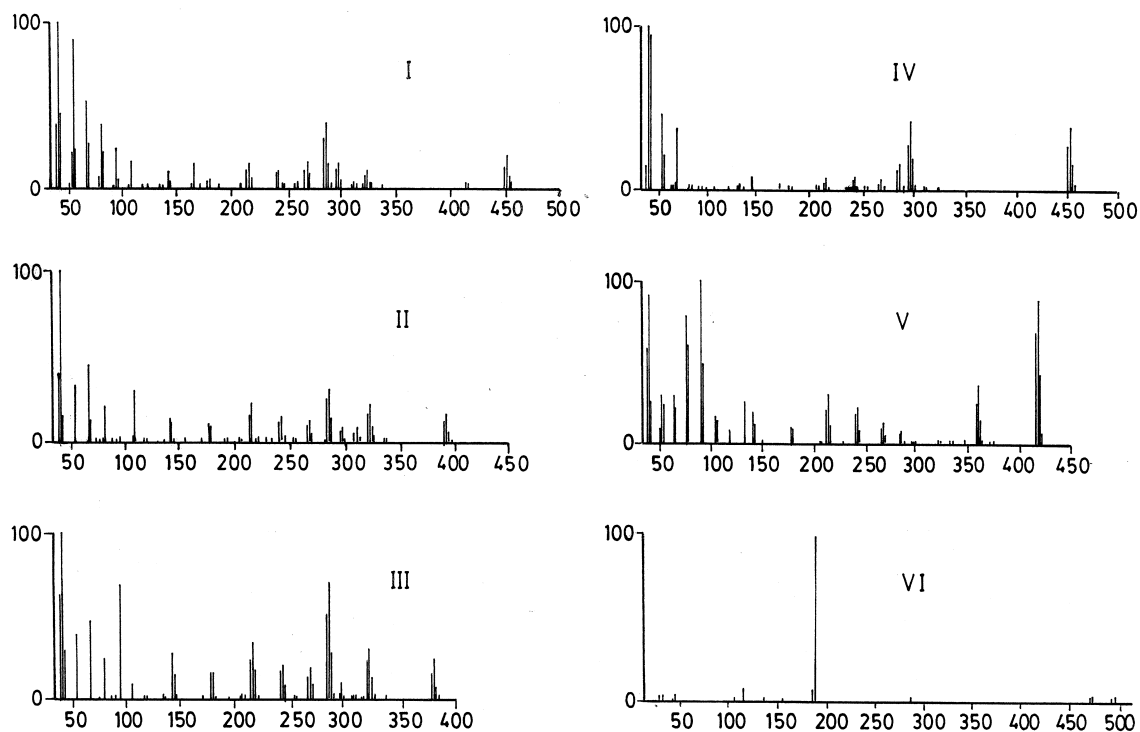

Fig. 3. EI-MS spectra of (1) *N*-cyclo-dodecyl tetrachlorophthalimide, (2) *N*-cyclo-octyl-tetrachlorophthalimide, (3) *N*-cyclo-heptyl-tetrachlorophthalimide, (4) *N*-dodecyl-tetrachlorophthalimide, (5) *N*-adamantyl-tetrachlorophthalimide, and (6) *N,N*-dihexyl-tetrachloro-phthalimic acid (LIMS).

Table 2
GC retention data

S. No.	Imide	Retention time t_R (min)	Relative retention time	Capacity factor k^1
1.	CDTCP	7.74	1.00	3.18
2.	COTCP	4.35	0.56	1.35
3.	CHTCP	3.53	0.45	0.90
4.	DTCP	4.67	0.60	1.52
5.	DHTCP	2.33	0.30	0.26
6.	ATCP	7.08	0.91	2.82

Table 3
GC-ECD detector response data

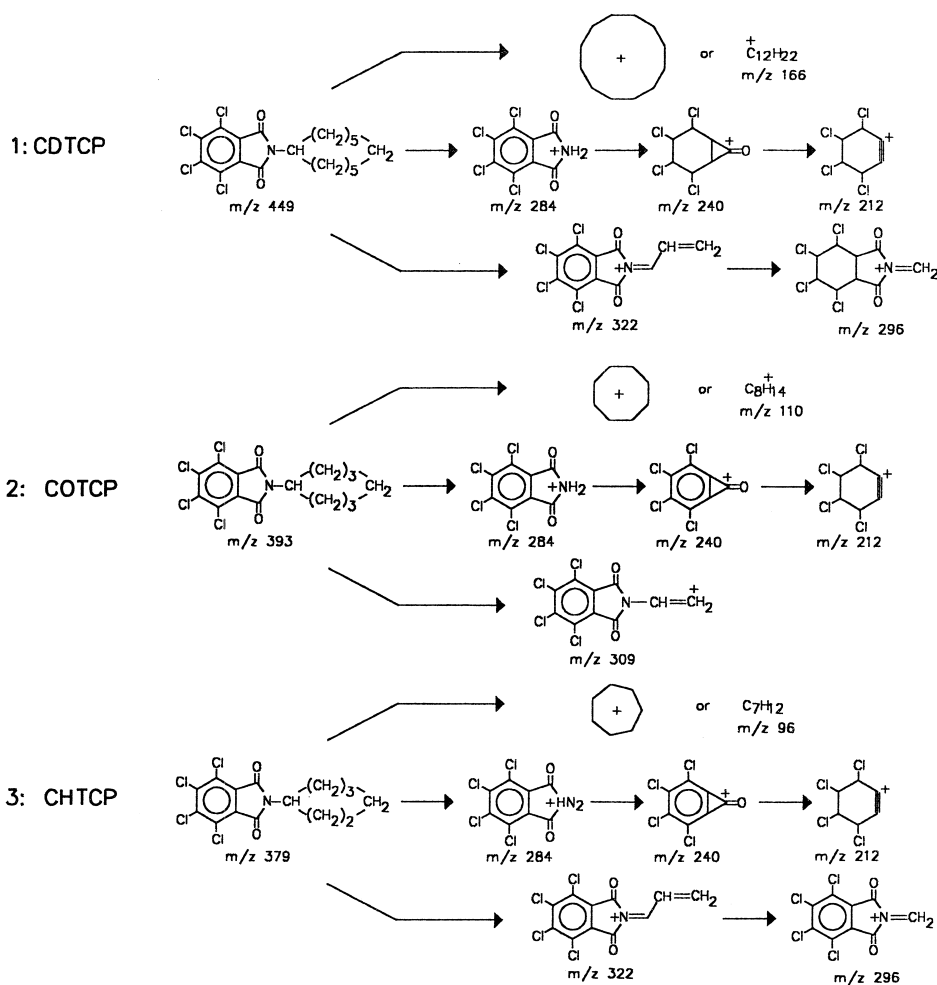| S. No.	Imide	Amount (μg)	Area	Relative response	% RSD
1.	CDTCP	1.0	1703206	1.24	1.54
2.	COTCP	1.0	4916048	3.58	0.96
3.	CHTCP	1.0	5569847	4.06	0.89
4.	DTCP	1.0	2719133	1.97	1.73
5.	DHTCP	1.0	2205337	1.59	1.85
6.	ATCP	1.0	1380214	1.00	1.92

Fig. 4. Mass spectral fragmentational pattern of cyclic imides.

tic compounds. It could be seen from Fig. 2 that all the compounds are well separated under the conditions used and the peaks are with excellent symmetry and reproducibility. The retention times (t_R), and capacity factors (k^1) are recorded in Table 2. The standard deviation in retention times is found to be ± 0.4 min. The retention data has been used for preliminary identification of imides in unknown samples.

Solutions of the six imides and their mixtures in methanol in concentrations of 0.1, 1.0, 10, 50, and 100 ng/μl were prepared and chromatographed. The linearity between the mass and integral response was checked. Calibration curves were drawn and found linear. All peaks were quantified by peak area. The

data was also subjected to regression analysis and correlation coefficients were calculated. The correlation coefficients were higher than 0.90 in all cases. The measured amounts have agreed well with the actual values to within 1.59%. The relative response factors obtained using electron capture detector are given in Table 3.

Two types of detection techniques viz: GC-ECD and GC–MS for determination of cyclic imides were tested. It could be seen from Fig. 3 that the spectra obtained using MS in the electron impact mode contain many fragments with low intensity. Therefore, quantification of trace amounts of the analytes using this technique was avoided. However, the fragmentation pattern was found to be quite indis-
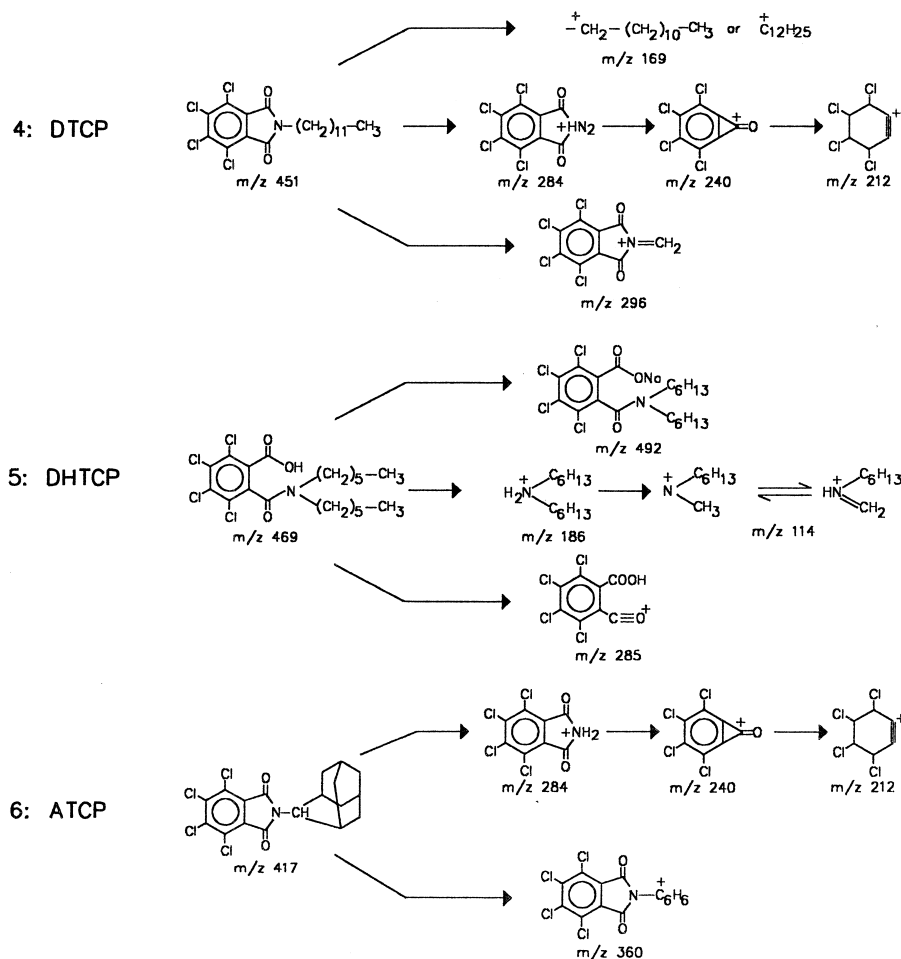

Fig. 4. (*continued*)

pensable for unambiguous identification of these compounds by GC–MS. Fig. 4 gives the fragmentation pattern of all the imides used in the present study. The fragments at m/z 284, 240 and 212 are found to be the characteristic ions of all the imides except DHTCP. In the case of DHTCP a slightly different pattern i.e, m/z 285, 186 and 114 was noticed. These fragments correspond to the loss of long chain hydrocarbons from the respective molecules and are the most characteristic parameters for their identification. Table 4 gives the characteristic M^+ and M^- ions with their relative abundances for all the imides. These molecules can never be mistaken with others because their mass spectra contain weak molecular ions with distinctive isotopic patterns. These clusters correspond to ^{35}Cl and ^{37}Cl isotopes of four chlorine atoms substituted in the aromatic ring of the phthalimide moiety. The pattern of M^+, M+2, M+4 and M+6 ions in the ratio of (11:14:7:1) is another characteristic parameter useful for identification of tetrachloropthalimides by GC–MS. ECD was chosen as an alternative technique not only for confirmation purposes but also quantification.

Known amounts of imides mixed with epoxy/alkyd resins were subjected to thermal treatment at 300°C in the laboratory. The treated material was dissolved in methanol and analysed by GC-ECD and GC–MS. A typical chromatogram of the methanolic

extract of the overheated imides is shown in Fig. 5. It represents the GC-ECD chromatogram of a methanolic extract of the 300°C thermally treated alkyd resin containing 2.5% each of COTCP and CDTCP. The concentration of each imide in different synthetic formulations was determined and the results are recorded in Table 5. It could be seen from Table 5 that the variation in the amount of imide detected, indicate that the rate of thermal evaporation for different compounds varies significantly. However, it has no affect on the reliability of detecting hot spot temperatures inside the generators. The important aspect of these studies was to model the heating environment inside the generators. It gives not only an indication regarding the temperature to which the imide was heated, but also the rate at which the electrical and mechanical strength is decreased simultaneously. Experiments were conducted in a closed atmosphere not only to restrict the aerial oxidation but also the loss of degradation products.

The general strategy for the analysis of cyclic imides consisted of the two-steps viz: (i) detection, and (ii) characterisation. The present approach to this strategy is to detect the intact molecules with GC-ECD and characterise them using electron-impact mass spectrometry (EI-MS). This approach has been applied successfully to monitor several of the power generators in service. For example a metal tab coated with a paint received from a power station was

Table 4
Characteristic mass spectral fragments and the molecular ions of imides

S. No.	Imide	M^+ ions (M+, M+2, M+4, M+6)	M^- ions (characteristic fragments)
1.	CDTCP	449 (14.1)[a], 451 (19.5) 453 (8.4), 455 (2.6)	322 (8.2), 296 (10.0), 284 (30.4) 240 (10.6), 212 (10.8), 166 (16.3)
2.	COTCP	393 (12.6), 395 (16.9) 397 (5.2), 399 (1.7)	322 (16.9), 309 (5.4), 284 (27.8) 240 (12.6), 212 (17.1), 110 (4.1)
3.	CHTCP	379 (15.1), 381 (23.6) 383 (6.5), 385 (1.5)	322 (22.1), 284 (49.5), 240 (16.5) 212 (22.8), 96 (30.8)
4.	DTCP	451 (27.6), 453 (36.1) 455 (17.0), 451 (2.1)	296 (17.4), 284 (13.2), 240 (6.3) 212 (4.2), 169 (38.2)
5.	DHTCP	470 (3.0), 472 (4.2) 474 (−), 476 (−)	492 (3.0), 287 (2.6) 186 (10.0) 114 (7.6)
6.	ATCP	417 (6.8), 419 (89.1) 421 (41.3), 423 (7.6)	360 (26.0), 284 (7.6) 240 (19.5), 212 (21.0)

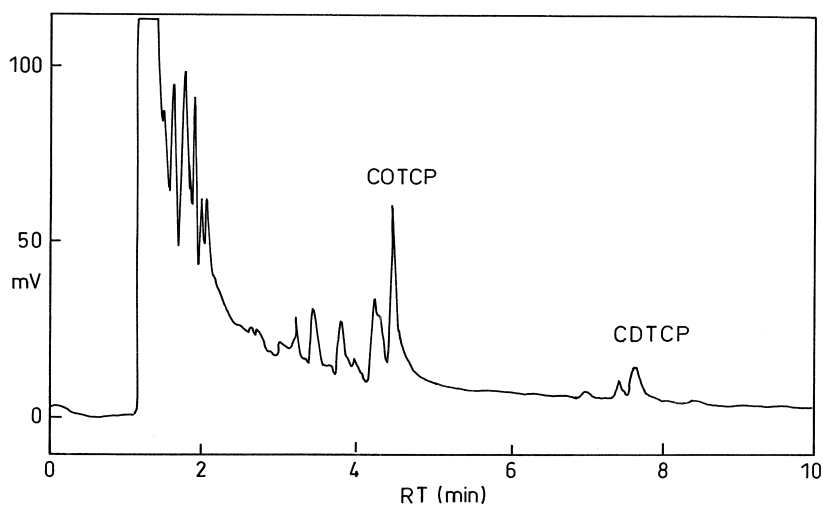[a] Values in parentheses are the % relative abundance.

Fig. 5. GLC chromatogram showing the presence of CDTCP and COTCP in a methanolic extract of a thermally evaporated synthetic formulation.

thermally treated and the extracted particulates were analysed using GC-ECD and GC–MS, simultaneously. Fig. 6 gives the GC chromatograms of the (A) alkyd resin blank and (B) 300°C thermally evapo-

rated products of the sample collected from the power plant and the tagging compound was identified based on agreement of retention time between the sample and a reference standard. Later it was

Table 5
Analytical data of synthetic formulations of imides thermally evaporated at 300°C

S. No.	Imide	Amount of imide in the coating medium (%)	Amount of imide thermally treated (μg)	Retention time t_R (min)	Molecular ion peak (M$^+$)	Area of corresponding peak	Amount of imide detected (μg)
1.	CDTCP	0.55	27.5	7.76	449	41437	24.25
2.	COTCP	0.55	28.6	4.33	393	93667	19.00
3.	DTCP	0.55	25.3	–	–	–	–
4.	DHTCP	0.55	28.0	2.32	470	34452	15.50
5.	ATCP	0.55	25.8	7.08	417	33547	24.25
6.	CDTCP	1.1	50.6	7.77	449	50907	29.75
7.	COTCP	1.1	49.5	4.36	393	13544	27.50
8.	DTCP	1.1	55.0	4.75	451	74792	27.50
9.	DHTCP	1.1	52.8	2.27	470	56505	25.50
10.	ATCP	1.1	50.6	7.04	417	51262	37.00
11.	CDTCP	2.20	112	7.72	449	169027	99.25
12.	COTCP	2.20	105.6	4.29	393	256610	52.00
13.	DTCP	2.20	112	4.65	451	153652	52.00
14.	DHTCP	2.20	114.4	2.24	470	118755	53.75
15.	ATCP	2.20	138.6	6.97	417	130232	94.25
16.	CDTCP	4.40	220	7.69	449	329210	193.25
17.	COTCP	4.40	215.0	4.29	393	404317	82.00
18.	DTCP	4.40	211.2	4.66	451	286445	105.25
19.	DHTCP	4.40	202.4	2.27	470	157867	71.50
20.	ATCP	4.40	308.0	7.06	417	337045	244.00

confirmed as CDTCP from the molecular ion fragmentation pattern obtained by GC–MS. The results are recorded in Table 6. This approach is useful in identifying the generators developing hot spots which may be further examined by alternative techniques. It is clear form these results that the method developed is simple, specific and suitable for not only monitoring the performance of generators in operation but also detecting the hot spots thereby averting catastrophic failures in advance.

Acknowledgements

Fig. 6. GLC chromatograms of methanol extracts of (A) alkyd resin blank and (B) an unknown sample collected from a power plant in India.

Table 6
Results of analysis of an unknown sample collected from a power plant

S. No.	Characteristic	Observation
1.	Color	Orange
2.	Amount of imide thermally treated	5 mg
3.	Temperature of heating	300°C
4.	Duration time	20 min
5.	Extracted solvent	Methanol
6.	Quantity of solvent	5.0 ml
7.	GC-retention time	7.45 min
8.	Area of corresponding peak	4005174
9.	Molecular ion peak	451
10.	Imide identified	CDTCP
11.	Quantity of Imide detected	0.294 (%)

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