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GASEOUS DEGRADATION PRODUCTS FROM THE PYROLYSIS OF INSULATING MATERIALS USED IN LARGE ELECTRICITY GENERATORS

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SUMMARY

Samples of insulating materials, typical of those used in large generators were pyrolysed at 700° in a hydrogen atmosphere and the products analysed by combined gas chromatography–mass spectrometry.

It is shown that the identification of a wide range of compounds is possible and that characteristic groupings and single compounds are produced from particular insulating materials.

Monitoring the generator cooling hydrogen for these products provides early warning that specific insulating materials within the generator are starting to degrade.

INTRODUCTION

Large electricity generators contain a number of organic insulating materials which may degrade to give gaseous products, either by ageing or because of electrical faults which produce hot spots or arcing. The value of gas analysis in the detection of faults in oil-filled transformers is well established[1]. Similar techniques can be applied to generators. By regular analysis of the hydrogen used for cooling the generator, impurities known to result from the degradation of a particular insulating material or from a specific degradation process can be identified. This may provide a valuable early warning of a developing fault. The method used for analyzing the cooling hydrogen for a wide range of possible insulation degradation products has been reported elsewhere[2].

Products which are characteristic of the degradation of a range of insulating materials at temperatures between 160 and 280° and for periods from 2 to 28 days have been reported[3]. This paper describes the results of degrading the same insulating materials for 10 sec at 700°. A temperature of 700° was considered to be realistic and consistent with typical generator fault temperatures and the need to produce sufficient amounts of degradation product to allow identification.

EXPERIMENTAL

The following insulating materials were studied in this work: epoxy-resin bonded mica; copal-resin bonded mica; high-temperature-resistant nylon paper;

phenolic-resin impregnated wood; press paper; asphalt-based core-plate varnish; lignin sulphonate-based core-plate varnish.

Small pieces of the insulating material were inserted into a disposable silica silica tube (25×2 mm I.D.) and held in place with ceramic wool. The silica tube, which was weighed before and after pyrolysis to determine the weight of material lost, was fitted in the coil probe of a Chemical Data Systems Pyroprobe 100 pyrolyzer. This in turn was fitted into the injector block of a Perkin-Elmer Model F30 gas chromatograph which was linked by a silicone-rubber membrane interface to a VG Micromass 12 mass spectrometer. The signal from the flame ionization detector of the gas chromatograph was recorded on a potentiometric recorder and the peak areas were measured using an Infotronics CRS 204 integrator. The degradation products were separated using Porapak Q and Tenax GC columns. Hydrogen was used as the carrier gas in both cases so that pyrolysis could occur in conditions as similar as possible to those occurring in a generator.

RESULTS

It is of value to determine the relative amounts of the degradation products found, in order to assess their potential as characteristic products. However, it is impractical to do this accurately, due to the difficulties involved in calibrating the chromatograph and the mass spectrometer for all the compounds present. Consequently the results are only semi-quantitative. Table I gives the relative amounts of degradation product as a convenient series of ranges, n, derived from the number of integrator counts, I, using the relationship $I \times 10^{-6} = 2^{n-1}$ *i.e.* $n = 1$ defines the range $0 < I \leqslant 10^6$, $n = 2$ defines the range $10^6 < I \leqslant 2 \times 10^6$ etc. The values of n range from 1 to 10. The integrator counts for unresolved peaks were apportioned using a method based on the relative size of the largest peaks in the mass spectrum of each compound.

DISCUSSION

Epoxy-resin bonded mica

Details of the manufacture and chemical nature of this material have been reported by Parriss[4]. Products resulting from the pyrolysis of various types of epoxy resin have been reported by Lee[5,6] who pyrolysed two resins at 350 and 450°; by Gac *et al.*[7] (450 to 800°); Bishop and Smith[8] (400 to 700°); Weigand and Hanna[9] (600°); Sakamoto *et al.*[10] (up to 290°); Andreev *et al.*[11] (200°) and Iglauer[12] (1000°). Their results are generally similar to the results of this work although in most cases only a small number of products were identified.

Bishop and Smith[8] pyrolysed two resins for 30 sec at 400, 500, 600 and 700°. In both cases the effect of increasing the pyrolysis temperature was to increase the amounts of pyrolysis products produced allowing a larger number of products to be identified. No compounds which were identified at a lower pyrolysis temperature were absent at a higher temperature. This would indicate that the main effect of increasing the pyrolysis temperature over this range is to increase the amount but not change the types of product produced.

Lee[5,6] and Bishop and Smith[8] give degradation schemes which explain the source of some of the products found. The low-molecular-weight hydrocarbons derive from the carbon chains in the molecule; the alkyl chlorides from residual epichlorohydrin used in epoxy manufacture; acraldehyde, acetaldehyde and acetone derive from the chains between the benzene rings. The other oxygen-containing alkyl compounds also probably derive from this source. Butanone is used as a solvent for the resin. Benzene and benzene substituted with hydroxyl and alkyl groups originate from the benzene rings and side chains in the polymer.

Copal-resin bonded mica

This material is manufactured from a processed blend of esterified natural copal resin, hydrocarbon resin and processed unsaturated oils (linseed, tung). The solvent is white spirit. The final product will consequently have a highly complex and indeterminate structure. The degradation products comprise primarily aromatic hydrocarbons, alkanes and alkenes. Aldehydes are of importance in this case, since three out of a total of five aldehydes found were not detected amongst the degradation products of the other materials studied. Small amounts of ethanol, acetone and cresol were also detected.

Nylon paper

This material has the general formula:

$$—(\text{-Ar-CO-NH-Ar-NH-CO-})_n—$$

where Ar represents a benzene ring with *meta* linkage. Iglauer[12] has reported the presence of benzene, aniline and toluene resulting from the pyrolysis of nylon paper at 1000°. In this work the major products were aniline, N,N-dimethyl acetamide, benzene and cyclohexene. Only a small amount of toluene was detected. Other products included small amounts of phenol, alkenes, 1,4-dioxan and acetic acid.

Phenolic-resin impregnated wood

This material is made by impregnating beechwood with a modified phenolic resin[13] which is cured by heat and pressure. The degradation products might be expected to be a mixture of those for the resin and the wood. Aromatic hydrocarbons and phenols have been shown to be typical of phenolic resin degradation at 700–750° by Zulaica and Guiochon[14]. Jackson and Conley[15] have studied the oxidative degradation of phenolic resins between 300 and 1000° and found little variation in the type of degradation product over a wide temperature range.

Goos and Reiter[16] have shown that oxygen-containing compounds such as alcohols, acids, aldehydes, ketones, esters and furans are all typical of wood degradation. In this work a large number of typical compounds from both resin and wood were found in the pyrolysis products.

Press paper

This material comprises some 99.5% cellulose. Wodley[17] has analyzed the degradation products of α-cellulose, pyrolyzed at 330° in nitrogen. His results are similar to this work in which a wide range of carbonyl compounds were found amongst the degradation products, together with alcohols and furans. A number of

TABLE I

DEGRADATION PRODUCTS

This table gives the relative amounts of degradation product as a convenient series of ranges, n, derived from the number of integrator counts I, using the relationship $I \times 10^{-6} = 2^{n-1}$, *i.e.* $n = 1$ defines the range $0 < I \leq 10^6$, $n = 2$ defines the range $10^6 < I \leq 2 \cdot 10^6$, etc. The compounds which have been underlined in the table uniquely or predominantly derive from one particular insulating material.

Degradation products: Name	Formula	Epoxy-resin bonded mica, Type 1	Epoxy-resin bonded mica, Type 2	Copal-resin bonded mica	Nylon paper	Phenolic-resin impregnated wood	Press paper	Asphalt-based core-plate varnish	Lignin sulphonate-based core-plate varnish
Methane	CH_4	5	7	3	1	4	3	7	8
Ethylene	C_2H_4	4	5	3	3	1	3	6	4
Ethane	C_2H_6	3	5	2	1	2	2	7	5
Hydrogen cyanide	HCN					1			3
Hydrogen sulphide	H_2S								1
Propylene	C_3H_6	7	9	3	1	1	3	8	4
Propane	C_3H_8			3	1	1	3	7	3
Formaldehyde	HCHO						3		
Methyl chloride	CH_3Cl	4	5		1	1			4
Dimethyl ether	CH_3OCH_3	1	4						4
Sulphur dioxide	SO_2								7
Methanol	CH_3OH	3	2			4	1	1	6
Acetaldehyde	CH_3CHO	7	8	3	1	4	4	7	3
Dimethyl disulphide	$(CH_3S)_2$								2
Butene	C_4H_8	1	2	4	1	2	3	6	3
Butane	C_4H_{10}		1	3	1	1	2	5	3
1,3-Butadiene	C_4H_6			4					
Ethyl chloride	C_2H_5Cl	3	5						
Ethanol	C_2H_5OH	3	5	1	1	1			
Methyl cyanide	CH_3CN				1	2		3	2
Propionaldehyde	C_2H_5CHO			4					
Furan	C_4H_4O			1		2	4	1	3

Acraldehyde	CH_2CHCHO	7	10	4		2	4	8	1
Pentene	C_5H_{10}			7	1			5	
Pentane	C_5H_{12}							5	2
Pentadiene	C_5H_8			3			1	6	1
Acetone	CH_3COCH_3	6	10	4		4	4	6	3
Propan-2-ol	$CH_3CH(OH)CH_3$					1			
Pyruvaldehyde	CH_3COCHO						5		
Cyclopentadiene	C_5H_6					1	1	3	
Allyl alcohol	CH_2CHCH_2OH	6	8						
Acetic acid	CH_3COOH	6	4		3	6	4	7	4
Methyl pyrrole	$C_4H_4NHCH_3$								4
3-Butenaldehyde	C_3H_5CHO						3		
Hexane	C_6H_{14}							7	
Carbon disulphide	CS_2								2
Butanone	$CH_3COC_2H_5$	8	8						
Hexene	C_6H_{12}			6	1			7	
Nitrobenzene	$C_6H_5NO_2$								2
Ethyl cyanide	C_2H_5CN					1			1
Methyl furan	$C_4H_3OCH_3$					3	5		5
Dimethyl sulphide	$(CH_3)_2S$								1
Vinyl acetate	$CH_3COOCHCH_2$					5			
Biacetyl	$C_4H_6O_2$					4	6		
Methyl formate	$HCOOCH_3$					1	5		
Methyl acetate	CH_3COOCH_3					4	4		2

(Continued on p. 90)

TABLE I (*continued*)

Degradation products: Name	Formula	Epoxy-resin bonded mica, Type 1	Epoxy-resin bonded mica, Type 2	Copal-resin bonded mica	Nylon paper	Phenolic-resin impregnated wood	Press paper	Asphalt-based core-plate varnish	Lignin sulphonate-based core-plate varnish
Methyl acrylate	$CH_2CHCOOCH_3$					3			
Methyl propionate	$C_2H_5COOCH_3$					3			
Methyl cyclopentadiene	$C_5H_5CH_3$			4		1	1	6	
Cyclohexene	C_6H_{10}			5	5		2	3	
Crotonaldehyde	$CH_3CHCHCHO$						3		
Propionic acid	C_2H_5COOH						3		
Benzene	C_6H_6	5		3	3	1	3	5	
Acetol	CH_3COCH_2OH		8			6	6		
Methyl isopropenyl ketone	$CH_3COC(CH_2)(CH_3)$						3		
Heptane	C_7H_{16}			2		1		6	
Dimethyl furan	$C_4H_2O(CH_3)_2$	5	5			1	3		3
1,4-Dioxan	$C_4H_8O_2$				1				
Heptene	C_7H_{14}			4	1			6	
n-Valeraldehyde	C_4H_9CHO			2					
2-Methoxyethyl acetate	$CH_3COOCH_2CH_2OCH_3$		6			4			
Pyrrole	C_4H_5N								3
Methylcyclohexane	$C_6H_{11}\cdot CH_3$			1				4	
Dihydropyran	C_5H_8O			4					
Octane	C_8H_{18}						1		

Toluene	$C_6H_5CH_3$	5	6	5	1	1	4	7	3
Octene	C_8H_{16}			2	1			7	1
Ester	R_1COOR_2					4			
Acetic anhydride	$(CH_3CO)_2O$					4			
Ester	R_1COOR_2					1			
Allyl acrylate	$CH_2CHCOOCH_2CHCH_2$		6						
Cyclohexanone	$C_6H_{10}O$							6	
Hexanaldehyde	$C_5H_{11}CHO$			2					
Ester	R_1COOR_2					5			
Ethyl cyclohexene	$C_6H_9 \cdot C_2H_5$			1				5	
Dimethyl pyrazole	$C_3H_2N_2(CH_3)_2$					1			
Dimethyl pyrrole	$C_4H_2NH(CH_3)_2$								3
Furaldehyde	C_4H_3OCHO					5	6		
Nonane	C_9H_{20}							6	
Furfuryl alcohol	$C_4H_3OCH_2OH$					2			
Nonene	C_9H_{18}			4	1			5	
Xylene	$C_6H_4(CH_3)_2$	8	5	4			2	7	2
Dimethyl pyrrole	$C_4H_2NH(CH_3)_2$								2
Xylene	$C_6H_4(CH_3)_2$		5	1				6	
N,N-Dimethylacetamide	$CH_3CON(CH_3)_2$				5				
Hydroquinone	$C_6H_4O_2$						2		

(Continued on p. 92)

TABLE I *(continued)*

Degradation products Name	Formula	Epoxy-resin bonded mica, Type 1	Epoxy-resin bonded mica, Type 2	Copal-resin bonded mica	Nylon paper	Phenolic-resin impregnated wood	Press paper	Asphalt-based core-plate varnish	Lignin sulphonate-based core-plate varnish
Styrene	$C_6H_5CHCH_2$			4			5	6	2
Dimethyl pyrrole	$C_4H_2NH(CH_3)_2$								2
Furyl methyl ketone	$C_4H_3OCOCH_3$						4		1
Hexahydroindene	C_9H_{16}			2					
Decane	$C_{10}H_{22}$							6	
Decene	$C_{10}H_{20}$			3	1			5	
Ester	R_1COOR_2					6			
Methylethyl benzene	$C_6H_4C_2H_5CH_3$			5			4	5	3
Methylethyl benzene	$C_6H_4C_2H_5CH_3$			4				5	
Trimethyl furan	$C_4HO(CH_3)_3$								2
Phenol	C_6H_5OH	7	9		1	6	3	6	4
Methyl furaldehyde	$C_4H_2O(CHO)(CH_3)$						4		
Benzofuran	$C_4H_3OC_6H_5$						4		1
Indan	C_9H_{10}							5	3
Methyl ethyl benzene	$C_6H_4C_2H_5CH_3$							6	
Aniline	$C_6H_5NH_2$				5				
Undecane	$C_{11}H_{24}$							6	
Undecene	$C_{11}H_{22}$			3				5	
Methyl styrene	C_9H_{10}			4					

Methyl styrene	C_9H_{10}			4					
Hydroxy methyl cyclopentenone	$C_5H_6O(CH_3)(OH)$						3		
Indene	C_9H_8			5			6	6	2
Cresol	$C_6H_4(OH)(CH_3)$		8	2	6			5	4
Dimethyl styrene	$C_{10}H_{12}$								2
Propyl benzene	$C_6H_5C_3H_7$			4					
Dodecane	$C_{12}H_{26}$							6	
Dodecene	$C_{12}H_{24}$							6	
Methyl benzofuran	$C_4H_2O(C_6H_5)(CH_3)$								1
Cresol	$C_6H_4(OH)(CH_3)$	6	9	1		8			2
Cyclohexenyl methyl ketone	$C_6H_9COCH_3$					6			
Cinnamaldehyde	$C_6H_5CHCHCHO$	6							
Dimethyl phenol	$C_6H_3(CH_3)_2(OH)$		7			8			3
Butenyl benzene	$C_6H_5C_4H_7$							6	
Pentyl benzene	$C_6H_5C_5H_{11}$							6	
Benzyl alcohol	$C_6H_5CH_2OH$					6			
Organosulphur									5
Tridecane	$C_{13}H_{28}$							6	
Tridecene	$C_{13}H_{26}$							6	
Methyl indene	$C_9H_7CH_3$						5	5	
Organo-sulphur									4

(Continued on p. 94)

TABLE I (*continued*)

Degradations products: Name	Formula	Epoxy-resin bonded mica, Type 1	Epoxy-resin bonded mica, Type 2	Copal-resin bonded mica	Nylon paper	Phenolic-resin impregnated wood	Press paper	Asphalt-based core-plate varnish	Lignin sulphonate-based core-plate varnish
Trimethyl phenol	$C_6H_2(OH)(CH_3)_3$					8			
Organo-sulphur									4
Tetradecene	$C_{14}H_{28}$							8	
Trimethyl phenol	$C_6H_2(OH)(CH_3)_3$					6			
Trimethyl phenol	$C_6H_2(OH)(CH_3)_3$					8			
Pentadecane	$C_{15}H_{32}$							8	
Pentadecene	$C_{15}H_{30}$							5	
Dimethoxy benzene	$C_6H_4(OCH_3)_2$						5		4
Dimethoxy benzene	$C_6H_4(OCH_3)_2$								6
Organo-sulphur									5
Hexadecane	$C_{16}H_{34}$						8		
Thymol	$(CH_3)C_6H_3CH(CH_3)_2(OH)$					7			
Heptadecane	$C_{17}H_{36}$							9	

aromatic compounds were also found. The presence of aromatic compounds was also reported by Wodley who deduced that they resulted from reactions between the initial products formed by breaking the cellulose molecule.

Asphalt-based core-plate varnish

This material is made by heating natural asphalt with linseed oil and other ingredients and dissolving the product in a mixture of solvents. The resulting varnish has a complex structure. The degradation products are primarily alkanes and alkenes with some aromatic hydrocarbons. Other products included some oxygen-containing compounds such as acraldehyde, acetic acid, acetone and cyclohexanone.

Lignin sulphonate-based core-plate varnish

This varnish is made from ammonium lignin sulphonate, a range of monosaccharides, furaldehyde, phosphoric acid and detergent (alkyl and aryl sulphonates). A wide range of compounds was identified in the degradation products. A number of organo-sulphur compounds were present, deriving from the sulphonate groups. Sulphur dioxide was also found. The nitrogen in compounds such as hydrogen cyanide, methyl and ethyl cyanides, nitrobenzene and pyrroles, present in the degradation products, probably derives from the ammonium ion in the raw materials. Other compounds present included furans, derived from the furaldehyde or the monosaccharides, hydrocarbons and methanol.

CONCLUSIONS

It is clear from the above discussion of the results that certain groups of compounds result from the degradation of particular insulating materials in hydrogen at 700°. It is also possible to pick out certain compounds which uniquely or predominantly derive from one particular insulating material. These compounds have been underlined in Table I and are listed as follows. Epoxy-resin: alkyl chloride, dimethyl ether, ethanol, allyl alcohol, butanone, allyl acrylate. Copal-resin: 1,3-butadiene, alkyl aldehydes, dihydropyran, methyl styrene, propyl benzene. Nylon paper: N,N-dimethyl acetamide, aniline. Phenolic-resin-impregnated wood: esters, acetic anhydride, benzyl alcohol, trimethyl phenol, thymol. Press-paper: pyruvaldehyde, butenaldehyde, crotonaldehyde, propionic acid, higher ketones, methyl furaldehyde, benzofuran. Asphalt-based core-plate varnish: alkanes, alkyl cyclohexane, cyclohexanone. Lignin-sulphonate-based core-plate varnish: sulphur dioxide, organosulphur compounds, pyrroles, carbon disulphide, nitrobenzene.

Monitoring the generator cooling hydrogen for these products may provide a warning of a developing fault since, although these results were obtained at 700°, the results of other workers[8,16] suggest that the same products are formed over a wide temperature range, with the amount of product increasing with increasing temperature.

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