*Thermochimica Acta*, 234 (1994) 127–137
Elsevier Science B.V., Amsterdam
*SSDI* 0040-6031(93)01512-2

# Study on the thermal degradation of varnishing systems for metallic paints applied in the automobile industry [1]

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(Received 9 November 1992; accepted 10 March 1993)

## Abstract

The results of investigations on the thermal stability of selected automobile finishing metallic lacquers are reported. Thermal analysis and pyrolysis techniques have been used to study the degradation behaviour and to determine the residual quantity of ash.

The samples were decomposed in air and additionally pyrolysed in nitrogen atmosphere at a tempeature of 450°C and different residence times by use of a modified Bayer–ICI–Shell (BIS) combustion apparatus. The qualitative and quantitative investigations of the decomposition or pyrolysis products were performed by gas chromatography–mass spectrometry (GC–MS).

## INTRODUCTION

In fully automated lacquering processes the workpieces have to be mounted on special carriers. During the process an undesired simultaneous coating of the carriers as thick layers cannot be avoided. To achieve good lacquering results on the workpieces the thick coatings of the carriers have to be removed.

From an environmental point of view and with respect to occupational safety and health the widely used devarnishing processes have to be substituted by methods which are more compatible for the environment and more protective for the workers. In addition the application of cryogenic [1–3] or thermal [4–11] devarnishing processes does not result in such great amounts of hazardous waste to be disposed of. Two different metallic coating systems used in the automobile industry were investigated to determine their thermal stability and the residual quantity of ash and to

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[1] Dedicated to Hans Georg Wiedemann.

identify the organic degradation products formed during the thermal treatment of the material.

## EXPERIMENTAL

### *Thermal analysis equipment*

The thermal analysis experiments were carried out by means of a Perkin-Elmer TGA 7/DSC 7 station.

### *Measuring conditions*

Weighed samples of 10 mg were used for the thermogravimetry (TG) and 2 mg for the differential scanning calorimetry (DSC) in a closed aluminium pan. An empty aluminum pan was inserted as a reference. The applied heating rates were in both cases 10 K $\mathrm{min}^{-1}$ from ambient temperature up to a final temperature of 900°C in case of the TG and 600°C for the DSC.

All samples were investigated in dynamic air and in dynamic nitrogen atmosphere.

### *Combustion apparatus*

The combustion experiments were carried out in a modified BIS apparatus which is described in more detail in ref. 12. A combination of XAD-4 and activated carbon tubes which were connected in series served as adsorption materials. The applied decomposition temperature was 450°C and the residence time ranged from 10 to 120 s. Acetone was used for desorbing the XAD-4 fraction and toluene for the desorption from activated carbon.

The first sample (see Table 2 below) was investigated in air and nitrogen atmosphere, while the last coating system was only decomposed in air atmosphere.

### *Qualitative and quantitative analysis*

For the qualitative and quantitative investigation we used a Hewlett Packard GC/MSD 5890/5970 system. The chromatographic experimental conditions are listed in Table 1.

TABLE 1

Chromatographic experimental conditions

| | XAD 4 Fraction (sample 1) | | Qualitative and quantitative chromatographic conditions | |
|---|---|---|---|---|
| | Qualitative | Quantitative | Charcoal desorbates | XAD 4 desorbates |
| Injection | Split | Splitless | Split | Splitless |
| Column | DB-1/0.25 μm/0.25 mm/60 m | SE-54/0.25 μm/0.32 mm/50 m | DB-1/0.25 μm/0.25 mm/60 m | Se-54/0.25 μm/0.32 mm/50 m |
| Carrier | Helium | Helium | Helium | Helium |
| Press/bar | 1.3 | 1.3 | 1.1 | 1.1 |
| Split/ml min$^{-1}$ | 15 | | 20 | |
| Slitless time/min | | 0.9 | | 0.9 |
| Sample quantity/μl | 1 | 1.6 | 1 | 1.6 |
| Injector temp./°C | 280 | 280 | 180 | 280 |
| Transfer line/°C | 280 | 280 | 280 | 280 |
| Temperature program | | | | |
| Start temp./°C | 60 for 16 min | 25 for 1 min | 40 for 5 min | 25 for 1 min |
| Heating rate/°C min$^{-1}$ | 6 to 280°C | 15 to 60°C | 10 to 280°C | 15 to 60°C |
| End temp./°C | 280 for 47 min | 60 for 2 min | 280 | 60 for 1 min |
| Heating rate/°C min$^{-1}$ | | 5 to 80°C | | 2.5 to 80°C |
| Heating rate/°C min$^{-1}$ | | 10 to 180°C | | 5 to 100°C |
| Heating rate/°C min$^{-1}$ | | 5 to 280°C | | 10 to 280°C |
| Solvent delay/min | 5 | 3 | 4 | 3.4 |
| Acquisition mode | SCAN mode ($m/z$ 33–500) | SIM mode | SCAN mode<br>$m/z$ 33–150 ($t \leq 13$ min)<br>$m/z$ 33–250 ($t > 13$ min) | SIM mode (quantitative)<br>SCAN mode (qualitative) |

### *Materials*

We have investigated two different metallic coating systems used in the automobile industry. The sample materials and their main applications are listed in Table 2.

TABLE 2

Sample materials

| No. | Base of mixture | Scope |
|---|---|---|
| 1 | Polyurethane (2 components) | Coating varnish for metallic paints |
| 2 | Melamine-acrylate | Coating varnish for metallic paints |

## RESULTS AND DISCUSSION

### *Thermal analysis*

The results obtained by the application of thermal analysis were compared with those from the BIS decomposition experiments. They are listed in Table 3.

In practice the varnishes will be embrittled at low temperatures and then mechanically removed for reasons of energy saving. As a result of the thermal analysis experiments it was evident that the decomposition temperatures of the lacquering systems had to be adjusted in the range from 300 to 500°C. Therefore varnish specimens (size $8 \times 50\,\text{mm}^2$) were thermally treated in the BIS apparatus in this temperature range and the results were checked by testing the scratch resistance. From these investigations the optimal temperatures were found to be in the range from 400 to 450°C.

TABLE 3

TA data

| Sample | $\Delta m/\%$ | $\text{DTG}_{\text{max}}/°\text{C}$ | $\text{DSC}_{\text{max}}/°\text{C}$ |
|---|---|---|---|
| Air atmosphere | | | |
| 1 | 2.5, 50, 17, 21, 9.5 | 191, 378, 446, 467, 593 | 265, 360, 419, 437 |
| 2 | 12, 45, 23, 19 | 269, 397, 411, 602 | 341, 388, 552 |
| Nitrogen atmosphere | | | |
| 1 | 48, 24, 25 | 387, 459, 481 | 398 [a], 469 [a] |
| 2 | 13, 75 | 276, 406 | 269 [a], 387 [a] |

[a] Endothermal.

TABLE 4
Quantity of residue

| Sample | Lacquer residue/% | |
|---|---|---|
| | TG | Pyrolysis |
| 1 | 36 | 19 |
| 2 | 19 | 18 |

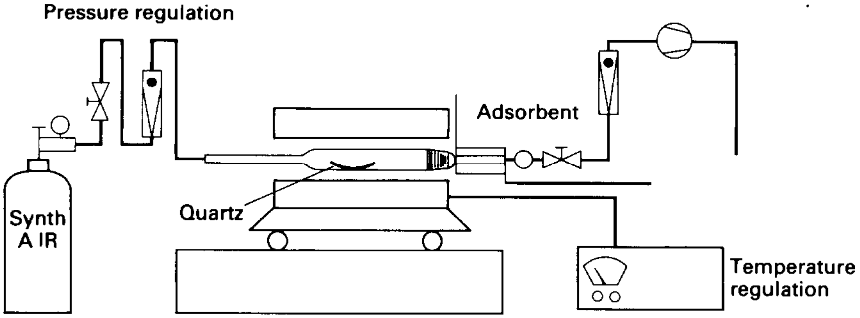

Fig. 1. Modified BIS apparatus.

For the determination of the lacquer residue a 50 mg weighed sample of the pure substance (quartz vessels) was burnt at 450°C in the BIS apparatus. The results are listed in Table 4 and compared with those from the TG experiments up to a temperature of 450°C (average value of the experiments in air and nitrogen atmosphere). Owing to the temperature programmed registration mode and the resulting different pyrolysis kinetics the values of the TG experiments are commonly higher than those of the pyrolysis experiments.

For the qualitative and quantitative determination of the decomposition products the samples were investigated in the modified BIS apparatus shown in Fig. 1) at 450°C in air and in nitrogen atmosphere at different residence times ranging from 10 to 120 s. The released decomposition products were adsorbed on a combination of XAD-4 resin and activated carbon tubes followed by desorption with acetone in the case of XAD-4 and toluene in the case of activated carbon fraction. The identification of the adsorbed components was achieved by means of GC–MS. The results for each coating system are given in the following text.

### *Two-component polyurethane varnish*

*XAD-4 fraction.* The sample, an isocyanate linked acrylate, was decomposed at several residence times between 10 and 120 s in air and in nitrogen atmosphere at 450°C. In Fig. 2 the TICs of the investigations in air

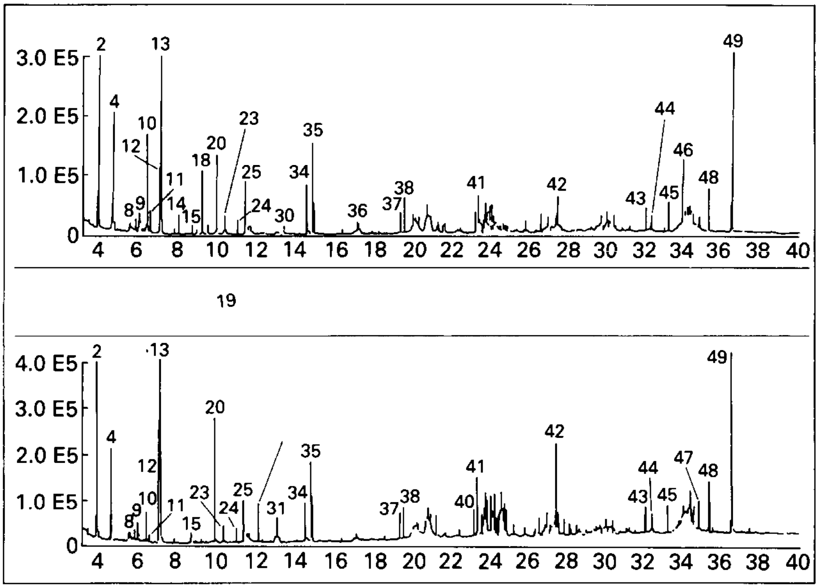

Fig. 2. Total ion chromatograms of polyurethane varnish in air and in nitrogen atmosphere.

and nitrogen atmosphere at a residence time of about 60 s are given. Since the recorded chromatograms are quite similar at different residence times the identified products and the corresponding peak numbers in Table 5 refer to these chromatograms. The main products of the thermal decomposition of the PUR-coating (sample 1 of Table 2), methylmethacrylate and styrene, are depolymerisation products. Also the formation of methylstyrene is based on this reaction. Oxidized compounds such as styrene oxide and benzaldehyde can be detected in air atmosphere. The

TABLE 5

Identified products in the XAD-4 fraction

| Peak no. | Substance | Peak no. | Substance |
|---|---|---|---|
| 2 | Methylmethacrylate | 19[a] | $C_3$-Benzene |
| 4 | Toluene | 20 | $\alpha$-Methylstyrene |
| 8 | Acetone impurity | 21 | Benzonitrile |
| 10 | Ethylbenzene | 23 | 1,2,4-Trimethylbenzene |
| 11 | Xylene (meta or para) | 25 | (2-Hydroxyethyl)-methacrylate |
| 12[a] | 2,6 Dimethylpyridine | 26[a] | $C_3$-Benzene |
| 13 | Styrene | 30 | Styrene oxide |
| 14 | Cumol | 32[a] | $C_3$-Benzene |
| 15[a] | $\beta$-Methylstyrene | 35 | *n*-Undecane (internal standard) |
| 18 | Benzaldehyde | | |

[a] Not verified by reference substance.

TABLE 6

Quantity (mg substance per g varnish) of identified products in the XAD-4 fraction

| Peak no. | Air atmosphere residence time/s | | | | | Nitrogen atmosphere residence time/s | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 10 | 15 | 30 | 60 | 120 | 10 | 15 | 30 | 60 | 120 |
| 2 | 3.054 | 3.605 | 3.893 | 3.597 | 3.351 | 1.948 | 2.606 | 2.906 | 2.520 | 2.955 |
| 4 | 0.382 | 0.662 | 0.678 | 0.365 | 0.455 | 0.395 | 0.454 | 0.543 | 0.498 | 0.560 |
| 10 | 0.287 | 0.529 | 0.465 | 0.113 | 0.237 | 0.211 | 0.220 | 0.281 | 0.248 | 0.207 |
| 11 | 0.161 | 0.198 | 0.186 | 0.150 | 0.177 | 0.100 | 0.085 | 0.229 | 0.157 | 0.056 |
| 13 | 5.687 | 5.862 | 6.071 | 5.526 | 3.893 | 6.807 | 7.179 | 7.230 | 7.272 | 6.856 |
| 14 | 0.073 | 0.105 | 0.100 | 0.074 | 0.064 | 0.021 | 0.035 | 0.027 | 0.023 | 0.030 |
| 18 | 0.926 | 0.923 | 1.100 | 1.811 | 2.059 | [a] | [a] | [a] | [a] | [a] |
| 20 | 0.278 | 0.482 | 0.471 | 0.140 | 0.177 | 0.962 | 1.004 | 1.043 | 1.074 | 0.959 |
| 21 | <0.01 | <0.01 | <0.01 | <0.01 | 0.121 | [a] | [a] | [a] | [a] | [a] |
| 22 | <0.01 | <0.01 | <0.01 | <0.01 | 0.249 | [a] | [a] | [a] | [a] | [a] |
| 23 | 0.059 | 0.101 | 0.073 | [a] | [a] | 0.194 | 0.269 | 0.392 | 0.304 | 0.118 |
| 25 | 3.908 | 3.719 | 4.121 | 4.111 | 3.495 | 3.391 | 3.987 | 3.622 | 3.825 | 3.573 |
| 30 | <0.01 | <0.01 | 0.067 | 0.317 | 0.743 | [a] | [a] | [a] | [a] | [a] |

[a] Not detected.

formation of benzonitrile, the $C_3$-benzenes, ethylbenzene, toluene, xylene and derivatives of pyridine has been described earlier [13–16].

Further, the formation of (2-hydroxyethyl)-methacryalte has to be mentioned. Since the use of hydroxyalcylated acrylates is typical for baking varnishes it can also be regarded as a depolymerisation product. Additional phenol can be detected from the pyrolysis in air atmosphere. Its concentration increases with the residence time. The formation of phenol from the decomposition of polyurethane has also been described elsewhere [17–22].

The results of the quantitative investigations in air and in nitrogen atmosphere are listed in Table 6.

*Activated carbon desorbates.* Most of the substances indicated in Fig. 3 could be identified by mass spectrometric analysis. As can be seen from Table 7 only simple aliphatic compounds such as butene and hexene were found as the main products. The results from the quantitative investigations are listed in Table 8 and show a decrease of the quantity of propene and butene in air and in nitrogen atmosphere with the residence time due to the incomplete adsorption of these substances under the given conditions.

### *Melamine-acrylate varnish*

*XAD-4 fraction.* This material was investigated only in air atmosphere at 450°C at a residence time of about 60 s. The total ion chromatogram of

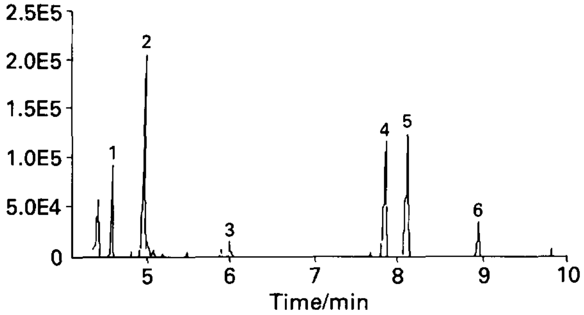

Fig. 3. Chromatogram of activated carbon desorbate.

TABLE 7

Identified products in activated carbon desorbate

| Peak no. | Substance | Peak no. | Substance |
|---|---|---|---|
| 1 | Propene | 4 | 1-Hexene |
| 2 | Butene | 5 | Hexane |
| 3 | pentane | | |

TABLE 8

Quantity (mg substance per g varnish) of identified products in activated carbon desorbate

| Peak no. | Air atmosphere residence time/s | | | | | Nitrogen atmosphere residence time/s | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 10 | 15 | 30 | 60 | 120 | 10 | 15 | 30 | 60 | 120 |
| 1 | [a] | [a] | 0.041 | 0.085 | 0.112 | [a] | [a] | 0.016 | 0.066 | 0.105 |
| 2 | 0.130 | 0.132 | 0.164 | 0.154 | 0.164 | 0.089 | 0.145 | 0.141 | 0.136 | 0.164 |
| 3 | [a] | 0.019 | 0.018 | [a] | [a] | [a] | [a] | [a] | [a] | [a] |
| 4 | 0.018 | 0.017 | [a] | [a] | [a] | 0.019 | <0.01 | [a] | [a] | [a] |
| 6 | 0.298 | 0.196 | 0.099 | 0.042 | 0.035 | 0.267 | 0.309 | 0.103 | 0.020 | 0.029 |
| 7 | 0.093 | 0.081 | 0.030 | <0.01 | [a] | 0.068 | 0.047 | 0.063 | [a] | [a] |
| 8 | 0.036 | 0.029 | <0.01 | [a] | [a] | [a] | [a] | [a] | [a] | [a] |

[a] Not detected.

the degradation in air atmosphere is given in Fig. 4 and the identified substances with its corresponding peak numbers are listed in Table 9.

The main products of the thermal degradation are methylmethacrylate, styrene and methacrylic acid isobutylester. These compounds are

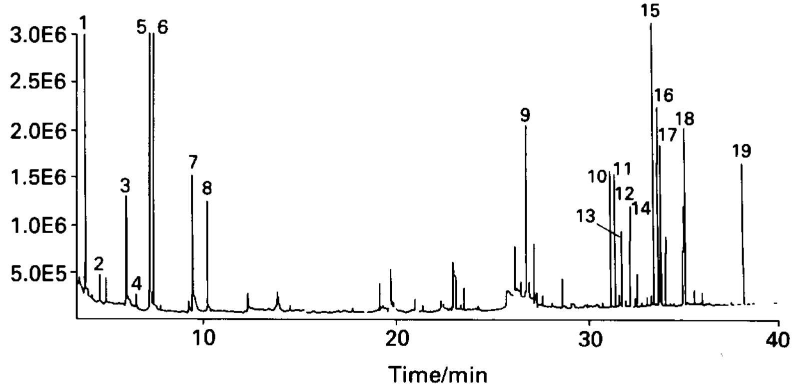

Fig. 4. Chromatogram from decomposition in air.

TABLE 9

Identified products for XAD-4 fraction

| Peak no. | Substance | Peak no. | Substance |
|---|---|---|---|
| 1 | Methylmethacrylate | 6[a] | Methacrylic acid isobutylester |
| 2 | Toluene | 7 | Benzaldehyde |
| 3 | Impurity of acetone | 8 | $\alpha$-Methylstyrene |
| 4 | Xylene (meta or para) | 18 | Dioctylphthalate |
| 5 | Styrene | | |

[a] See Table 5.

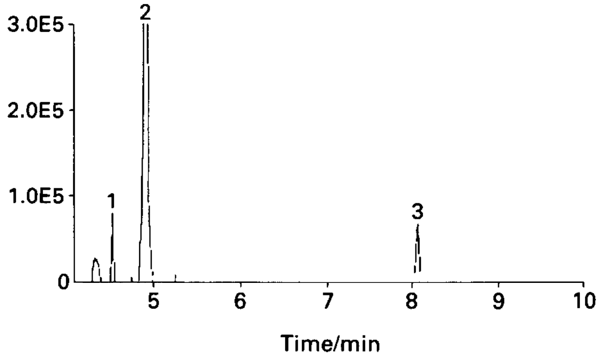

Fig. 5. Chromatogram of the desorbate of the activated carbon fraction.

monomers from the acrylate resin, regenerated by the depolymerisation reaction of the resin. The formation of $\alpha$-methylstyrene is based on the monomers, while benzaldehyde is formed by the oxidation of styrene. In addition the plasticizer dioctylphthalate was detected. A great part of the

TABLE 10

Identified products for activated carbon desorbate

| Peak no. | Substance |
|---|---|
| 1 | Propene |
| 2 | Butene |
| 3 | Hexane |

pyrolysis products consists of high boiling components, probably formed during the statistical cleavage of the macromolecules, but a recombination of smaller fragments in the gas phase cannot be excluded. The identification of these fragments by GC–MS could not be performed.

*Activated carbon desorbates.* From the activated carbon desorbates only simple aliphatic compounds could be detected. In Fig. 5 the chromatogram is shown and Table 10 and the identified products are listed.

## SUMMARY

(1) The investigations have shown that the thermal process is a useful alternative to the common devarnishing techniques. With respect to energy use and the combination of thermal and mechanical processes the optimal temperature was found to be 400–450°C.

To avoid combustion or fulmination of the organic matter, which constitutes approximately 10% of the coating material, an oxygen reduced atmosphere is required for the thermal process.

(2) A thermal treatment of the pyrolysis gases (after burning) will on the one hand reduce the amount of organic matter and on the other provide energy for the pyrolysis process. With respect to the "TA-Luft" the exhaust gases have to be monitored and the amount of organic matter has to be reduced. Since we have investigated only simple varnishing systems without any organic or inorganic pigments, in practice the emission of inorganic compounds from these additives has to be monitored.

(3) The investigations have shown that in the case of polyurethane no isocyanates will be found in the gas phase. Therefore monitoring of these substances will not be necessary.

## REFERENCES

1 A. Köhler, Oberfläche JOT, 9 (1984) 28–32.
2 R. Schaub and G. Böhlen, Seminar Lackalternativen 83, Bad Nauheim, 1982.
3 Rump, K. Fachbroschüre Oberflächentech., 5 (1985) 56–58.
4 R. Fronek, Metalloberfläche, 3 (1985) 77–112.

5 R. Fronek, Oberfläche JOT, 5 (1986) 39–41.
6 R. Fronek, Fachkongreß "Lackalternativen 1984", Basel 1984.
7 Eisenmann Umwelttechnik, Firmenschrift UT 16.
8 Schwing Verfahrenstechnik, Firmenschrift.
9 Strunz, Firmenschrift Ges. f. Verf. u. Entsorgungstechnik mbH.
10 H. Uher, Fachbroschüre Oberflächentechn., special issue.
11 J. Halbartschlager, VDI-series 3, 109, Düsseldorf, 1985.
12 Stoffers, H. Dissertation, Paderborn, 1990.
13 I.C. McNeil, T. Straiton and P. Anderson, J. Polym. Sci. Polym. Chem. Ed., 18 (1980) 2085.
14 G. Camino, N. Grassie and I.C. McNeill, J. Polym. Sci. Polym. Chem. Ed., 16 (1978) 95.
15 N. Grassie, I.C. McNeil and J.N.R. Samson, Eur. Polym. J., 14 (1978) 931.
16 A. Hamoudi and I.C. McNeill, Eur. Polym. J., 14 (1978) 525.
17 S.H. Kandil, A. El-Kholy, M. El-Shirbiny and Z. El-Sheikh, Polym. Degrad. Stab., 4 (1988) 349.
18 K.T. Joseph and R.F. Browner, Anal. Chem., 52 (1980) 1083.
19 W.D. Wooley, Br. Polym. J., 4 (1978) 27.
20 B.C. Levin, Fire Mater., 11 (1987) 143.
21 H.J. Petajan, et al., Science 187 (1975) 742.
22 M. Paabo and B.C. Levin, Fire Mater., 11 (1987) 1.