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Volatiles Released During Low Temperature Heating of Zepel RN.

AUTHOR: R. P. Lattimer Brecksville R&D Center D/8510 June 19, 1986
R. E. Harris

TO: M. B. Lattimer Brecksville R&D Center D/8526 6FD10D2

SUMMARY

The volatiles released during low temperature heating of Zepel RN are mostly residuals from polymerization (i.e., monomers, alcohols and associated fluorine-containing chemicals). The Zepel RN "monomer" is oligomeric; it has been identified as 1H,1H,2H,2H-perfluoroalkyl methacrylate. As you suspected, Zepel RN has excellent potential as an Early Warning Effect additive for use in PVC wallcoverings.

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SAMPLE IDENTIFICATION



9-1. A Zepel[R] RN dried film. (Zepel RN is a DuPont fluorine-containing polymer.)

PROBLEM DEFINITION

You are studying "early warning" fire protection systems for BFG Koroseal[R] wallcoverings. This work is related to information contained in a recent Westinghouse patent.[1] Westinghouse claims that materials containing DuPont's Zepel RN coating cause activation of an ionization type smoke/fire alarm during early stages of sample heating (~50-200°C). This early detection can only be caused by the release of volatile chemicals from the sample that are capable of activating the alarm.

The first report in this series showed that Zepel RN releases numerous volatile chemicals at temperatures <200°C, including numerous "fluoropolymer fragments."[2] You requested that we examine these volatiles in more detail to obtain a better characterization of the evolved chemicals so that you could assess toxicity and subsequent manufacturing effects.

EXPERIMENTAL APPROACH

The Zepel RN material is quite complex chemically, so a number of mass spectral approaches were used. One technique used was GC-MS analysis of an acetone extract of the dried Zepel film. Both electron impact (EI-MS, 70eV) and chemical ionization (CI-MS, isobutane reagent gas) were used at low mass resolution. This approach has the advantage that the chemical components are separated prior to mass spectral analysis.

A second approach that was used is high resolution (or atomic composition) mass spectrometry. In this, the mass of a particular ion is measured accurately to three or four decimal places. This enables one to determine, normally unambiguously, the atomic composition (i.e., the elemental formula) for the ion. This provides a very powerful tool for structure elucidation of unknown chemicals.

A third approach that was used is the recently developed time/temperature profiling procedure.[3] In this, the sample is heated at a constant rate (5°C/min) at atmospheric pressure under helium flow. This method allows one to determine the temperature at which a particular chemical component starts to evolve from the sample.

RESULTS

A GC-MS trace of the acetone extract of Zepel RN is shown in Figure 1 with the peaks identified. It is quite clear from Figure 1 that the volatiles in Zepel RN are a very complex mixture of oligomeric chemicals. The peaks were identified from their EI and CI mass spectral fragmentation patterns. High resolution accurate mass measurements (Table I) were very instrumental in assigning the structures. The low temperature volatiles are almost exclusively fluorine-containing chemicals which can be grouped into five oligomeric series:

-- "A" series (monomers). $CH_2=C(CH_3)-COO-C_2H_4-C_{2n}F_{4n+1}$ MW 132 + 100n

MW = 432 - 532 - 632 - 732 - 832 - 932
n = 3 - 4 - 5 - 6 - 7 - 8

These are the Zepel RN residual monomers: 1H,1H,2H,2H-perfluoroalkyl methacrylates. Based on the patents you provided, DuPont suggests several possible monomers that can be used to make fluorinated acrylate polymers.[4-5] Methacrylate esters is one class of compound that is mentioned. One patent suggests, however, that the most common type of fluorinated alcohol may be 1H,1H-perfluoroalkyl.[4] This is in contrast to the actual alcohol that was found in Zepel RN, viz 1H,1H,2H,2H-perfluoroalkyl alcohol.

-- "B" series (alcohols). $HO-C_2H_4-C_{2n}F_{4n+1}$ MW = 64 + 100n

MW = 364 - 464 - 564 - 664 - 764 - 864
n = 3 - 4 - 5 - 6 - 7 - 8

These are the residual alcohols used in synthesis of the monomeric esters.

-- "C" series (ethers). $C_{2m}F_{4m+1}-C_2H_4-O-C_2H_4-C_{2n}F_{4n+1}$ MW 110 + 100(m+n)

MW = 610 - 710 - 810 - 910 - 1010 - 1110 - 1210
m+n = 5 - 6 - 7 - 8 - 9 - 10 - 11

These would be formed via self condensation of the alcohols.

-- "D" series (iodides). $I-C_2H_4-C_{2n}F_{4n+1}$ MW 174 + 100n

MW = 474 - 574 - 674 - 774 - 874 - 974
n = 3 - 4 - 5 - 6 - 7 - 8

These must be formed from some side reaction of the alcohols with an active iodide species.

-- "E" series (chlorides). $Cl-C_2H_4-C_{2n}F_{4n+1}$ MW 82 + 100n ($^{35}Cl$ isotope)

MW = 382 - 482 - 582 - 682 - 782
n = 3 - 4 - 5 - 6 - 7

Like the iodides, these must be formed from some side reaction in the manufacturing process. The exact molecular weights of the chloride oligomers detected by GC-MS (Figure 1) are not known, since no molecular ions could be observed either by EI or CI analysis.

Isobutane CI time/temperature profiles are given in Figures 2-4 for the monomers, alcohols and ethers, respectively. (Profiles could not be obtained for the chlorides and iodides since these did not yield CI $MH^+$ ions.) The key fact to be noted from these profiles is the wide range of volatilities of the chemicals released from Zepel RN. While some components evolve at the beginning of the experiment (30°C), others are not released until much higher temperatures (up to ~120°C) are attained.

CONCLUSIONS

1. Zepel RN is a polymer derived from 1H,1H,2H,2H-perfluoroalkyl methacrylate. The "monomer" is itself oligomeric, with molecular weights ranging from ~300-1000 amu.

2. The volatiles released from Zepel RN in the range ~30-150°C are almost exclusively residuals remaining from the polymerization process. These include fluorinated monomers, alcohols, ethers, chlorides and iodides. Minor amounts of other fluorine-containing residuals might also be present, but no other fluorine compounds were detected. The relative concentrations of the various oligomer series are not known. Fluorine compounds have widely different ionization efficiencies, so one cannot use the relative peak heights in Figure 1 to reliably estimate concentrations.

3. Our analysis confirms your hypothesis that Zepel RN should be very attractive as an Early Warning Effect additive for PVC wallcoverings, for two reasons. First, since the Zepel RN volatiles all contain multiple numbers of fluorine and/or oxygen atoms, the chemicals should be excellent activators of ionization type smoke/fire detectors. Second, the Zepel RN residuals span a wide range of volatilities. Thus even if some components are lost through evaporation during processing, other components would still be available to cause an Early Warning Effect.

4. It should be noted that the Zepel RN volatiles are released at much lower temperatures than the phthalate plasticizers which cause an Early Warning Effect in most commercial PVC wallcoverings. In our earlier study, the lowest temperature for evolution of any phthalate plasticizer was ~117°C,[3] while some Zepel RN residuals are detectable at room temperature or slightly above.

5. In an earlier report,[2] we noted some other volatile residuals in Zepel RN. These include ethylene glycol (EG), poly(ethylene glycol), palmitic and stearic acids, and a trace of dioctyl phthalate. In our time/temperature profiling experiments, only ethylene glycol was detected below a temperature of ~120°C. Ethylene glycol thus might contribute to an Early Warning Effect due to Zepel, but EG is so volatile that it would probably be lost from a wallcovering during processing, storage or end use. The other chemicals mentioned above are not volatile enough to contribute to an Early Warning Effect in the presence of the much more volatile fluorine-containing species.

R P Lattimer
Robert P. Lattimer

R. E. Harris
Robert E. Harris

Log Book Reference: Service Book 805, pp. 134-137; S. B. 817, pp. 1, 9-10; MS4957.

/gg
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cc: J. B. Pausch
R. S. Varga
E. A. Huettel (Marietta)
J. D. Mason (Marietta)
R & D Files

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1. L. N. Yannapoulos, R. D. Straw and D. C. Philips, U. S. Patent 4,520,157, May 28, 1985.

2. R. P. Lattimer. "Volatiles Released During Heating of a PVC Wallcovering and Coatings," Project 6IF10D2, December 18, 1985.

3. R. P. Lattimer, "Time/Temperature Profiling of Volatiles Released from PVC Wallcoverings," Project 6FD10D2, June 18, 1986.

4. R. E. Johnson, Jr. and S. Raynolds, U. S. Patent 3,256,230, June 14, 1966.

5. R. E. Johnson, Jr. and S. Raynolds, U. S. Patent 3,256,231, June 14, 1966.

Table I

Accurate Mass Measurements and Atomic Compositions of Zepel RN Volatiles

| Measured Mass[a] | Atomic Composition | Calculated Mass[b] | Ion Identity |
|---|---|---|---|
| 69.0341 | $C_4H_5O$ | 69.0340 | $CH_2=C(CH_3)-CO^+$ (monomer fragment) |
| 86.0368 | $C_4H_6O_2$ | 86.0368 | $CH_2=C(CH_3)-COOH^{+\cdot}$ (monomer fragment) |
| 113.0596 | $C_6H_9O_2$ | 113.0602 | $CH_2=C(CH_3)-COO-C_2H_4^+$ (monomer fragment) |
| 532.0306 | $C_{14}H_9O_2F_{17}$ | 532.0331 | Monomer $M^{+\cdot}$ (n = 4) |
| 632.0252 | $C_{16}H_9O_2F_{21}$ | 632.0267 | Monomer $M^{+\cdot}$ (n = 5) |
| 665.0028[c] | $C_{14}H_6OF_{25}$ | 665.0019 | Alcohol $MH^+$ (n = 6) |
| 764.9925[c] | $C_{16}H_6OF_{29}$ | 764.9955 | Alcohol $MH^+$ (n = 7) |
| 377.0194 | $C_9H_6OF_{13}$ | 377.0211 | $C_6F_{13}-C_2H_4-O-CH_2^+$ (ether fragment) |
| 477.0137 | $C_{11}H_6OF_{17}$ | 477.0147 | $C_8F_{17}-C_2H_4-O-CH_2^+$ (ether fragment) |
| 711.0234[c] | $C_{16}H_9OF_{26}$ | 711.0238 | Ether $MH^+$ (n = 6) |
| 811.0140[c] | $C_{18}H_9OF_{30}$ | 811.0174 | Ether $MH^+$ (n = 7) |

Table I (Con't)

Accurate Mass Measurements and Atomic Compositions of Zepel RN Volatiles

| Measured Mass[a] | Atomic Composition | Calculated Mass[b] | Ion Identity |
|---|---|---|---|
| 327.0038 | $C_8H_3F_{12}$ | 327.0043 | $(M - HFI)^+$ (n = 3) (iodide fragment) |
| 426.9977 | $C_{10}H_3F_{16}$ | 426.9979 | $(M - HFI)^+$ (n = 4) (iodide fragment) |
| 473.9154 | $C_8H_4F_{13}I$ | 473.9152 | Iodide $M^{+\cdot}$ (n = 3) |
| 573.9079 | $C_{10}H_4F_{17}I$ | 573.9088 | Iodide $M^{+\cdot}$ (n = 4) |
| 112.9962 | $C_3H_4F_2{}^{35}Cl$ | 112.9970 | $^{35}Cl\text{-}C_2H_4\text{-}CF_2^+$ (chloride fragment) |
| 114.9936 | $C_3H_4F_2{}^{37}Cl$ | 114.9940 | $^{37}Cl\text{-}C_2H_4\text{-}CF_2^+$ (chloride fragment) |

[a]Measured by peak matching at a resolution $M/\Delta M = 10000$. Electron impact mode unless otherwise stated.

[b]Based on the given atomic composition.

[c]Isobutane chemical ionization mode.

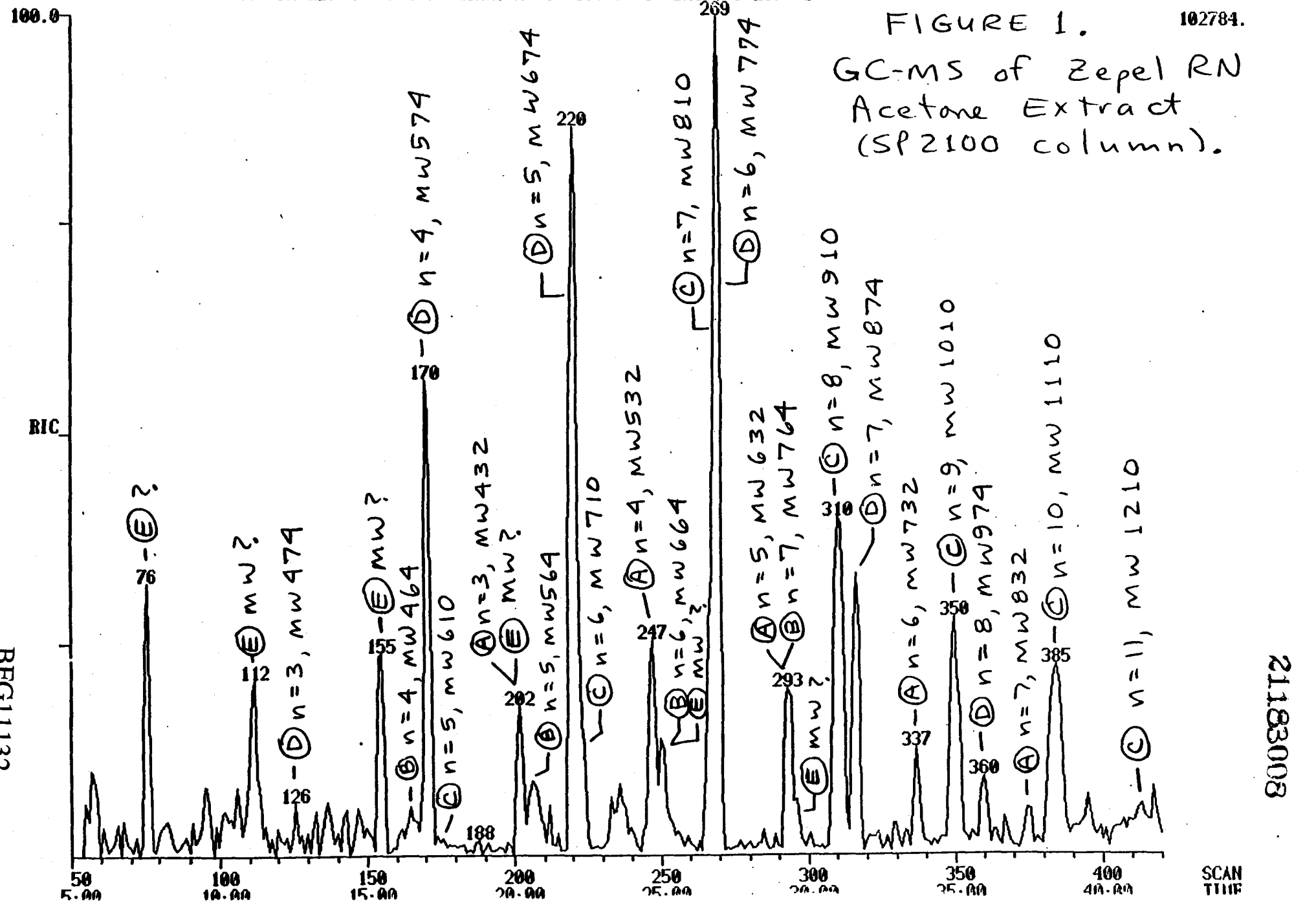


FIGURE 1.

GC-MS of Zepel RN Acetone Extract (SP2100 column).

102784.

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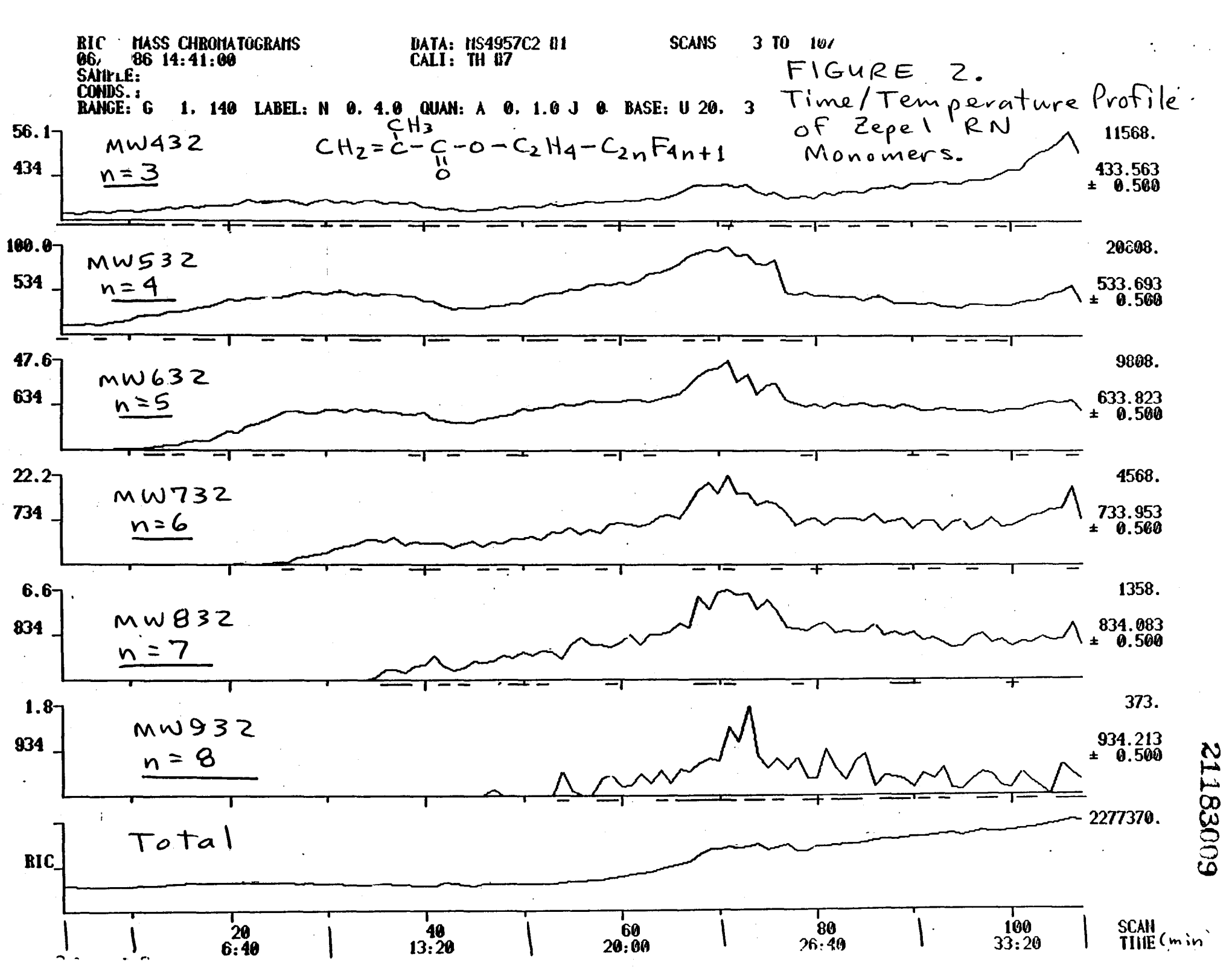
21183008




$$CH_2=C(CH_3)-C(=O)-O-C_2H_4-C_{2n}F_{4n+1}$$

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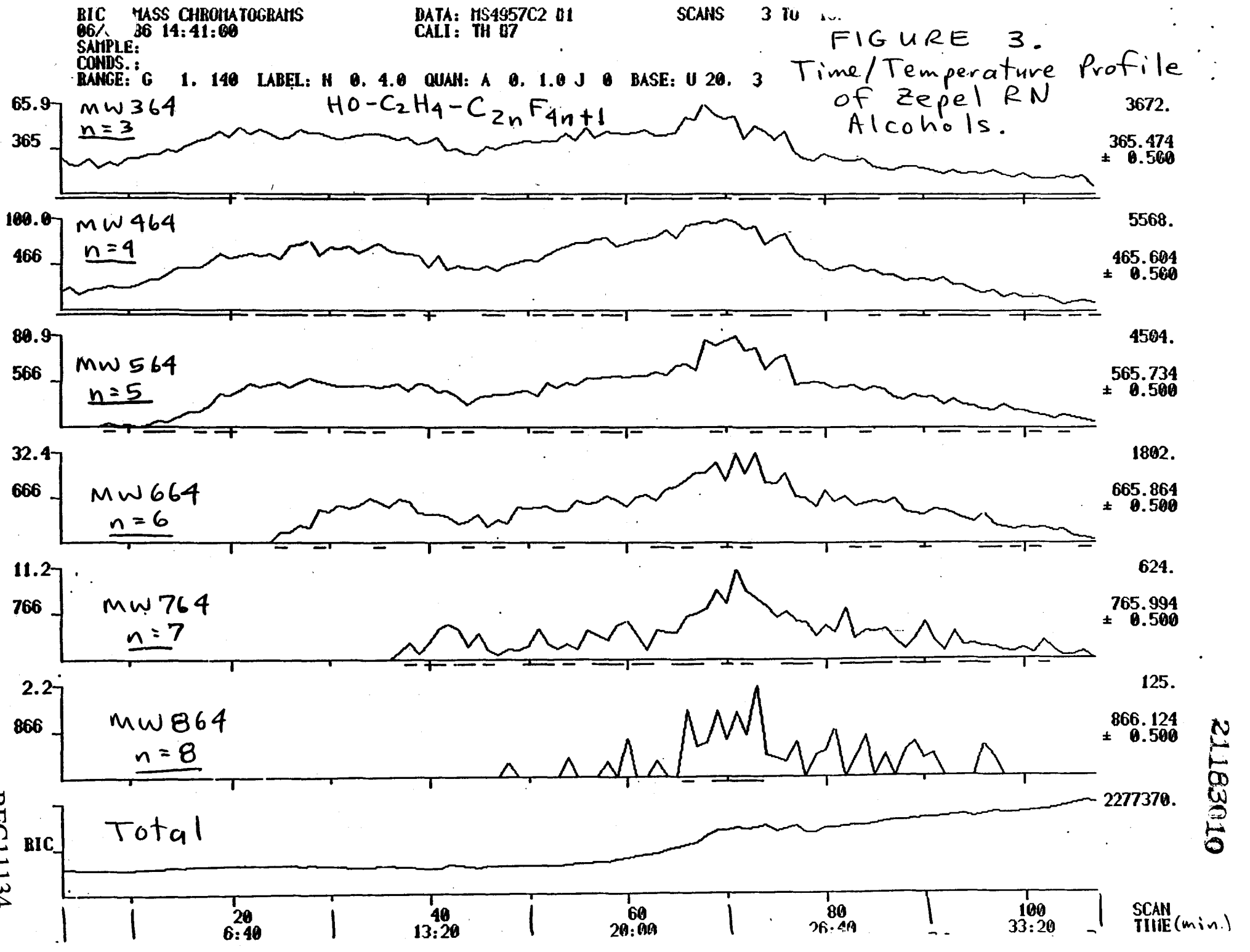
21183009


RIC MASS CHROMATOGRAMS
DATA: MS4957C2 01
SCANS 3 TO
06/ 36 14:41:00
CALI: TH 07
SAMPLE:
CONDS.:
RANGE: G 1. 140 LABEL: N 0. 4.0 QUAN: A 0. 1.0 J 0 BASE: U 20. 3
FIGURE 3.
Time/Temperature Profile of Zepel RN Alcohols.
65.9
365
MW364
n=3
HO-C2H4-C2nF4n+1
3672.
365.474
± 0.500
100.0
466
MW464
n=4
5568.
465.604
± 0.500
80.9
566
MW564
n=5
4504.
565.734
± 0.500
32.4
666
MW664
n=6
1802.
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± 0.500
11.2
766
MW764
n=7
624.
765.994
± 0.500
2.2
866
MW864
n=8
125.
866.124
± 0.500
RIC
Total
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13:20
60
20:00
80
26:40
100
33:20
SCAN
TIME(min.)
BFG11134
21183010

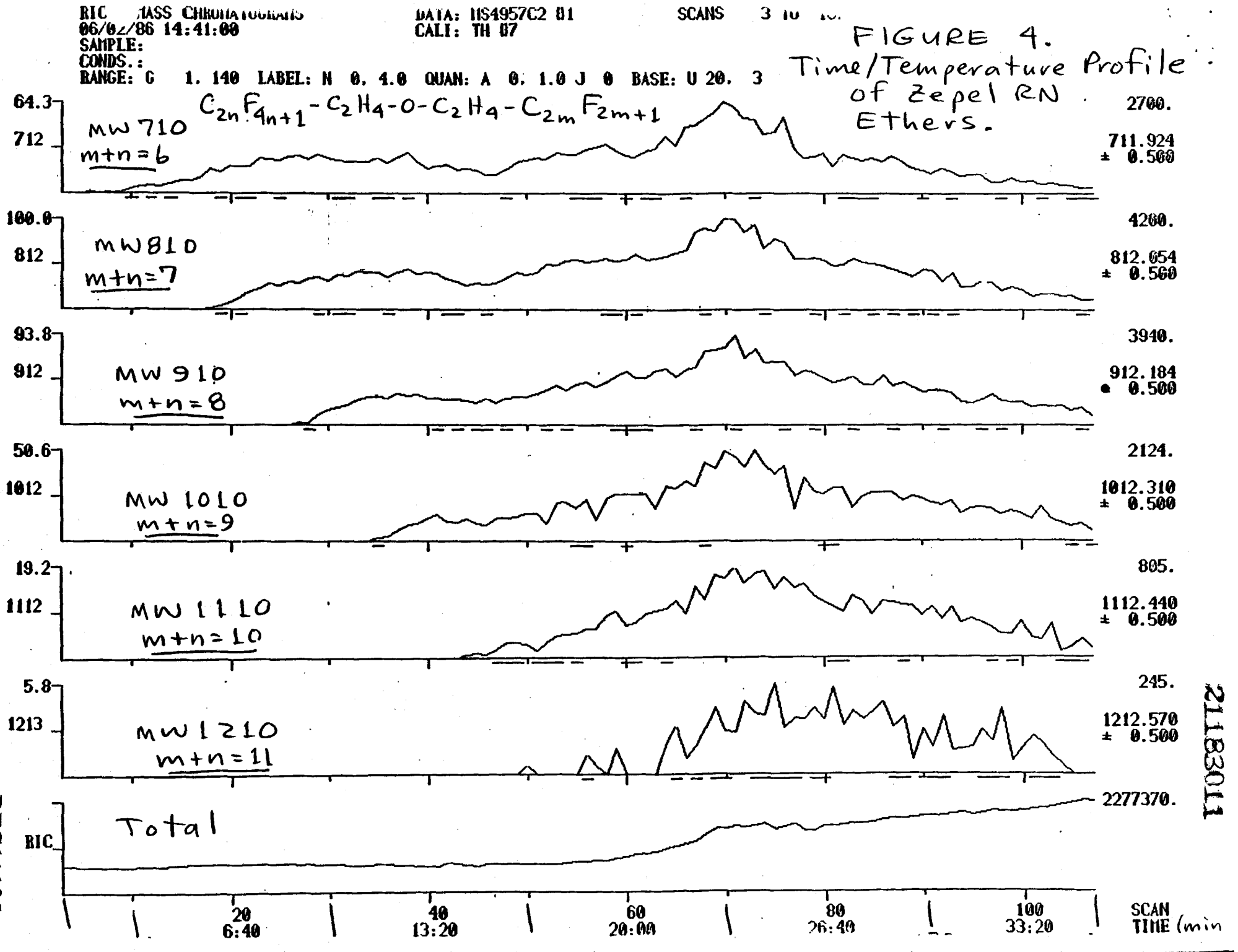


FIGURE 4.
Time/Temperature Profile of Zepel RN Ethers.

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