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# Modelling of Polymer Photodegradation for Solar Cell Modules

A Quarterly Technical Progress Report

Covering the period January 1 - March 31, 1981

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LSA Project, Technology Development Area

## Contract Goals and Objectives

As part of the Encapsulation Task, this research program is intended to model the photodegradation of synthetic polymers used as pottants and/or cover sheets in the LSA solar cell module designs. It involves the development of a computer simulation of the chemical processes that take place under weathering conditions which could, in principle, relate directly to the performance of these materials and afford some basis for predicting and/or controlling their useful lifetimes.

The program can be divided into three main parts:

1. The development of a computer program to model the weathering/photooxidation of an ethylene-vinyl acetate copolymer as a typical candidate for LSA applications.
2. The development of new analytical procedures for the determination of photooxidation and photodegradation at early stages in solid polymer samples.
3. The development of weathering tests suitable for use with a computer kinetic model to provide a basis for extrapolated predictions.

## Summary

### 1. Computer Simulation of Photooxidation

In the first year of the contract, a computer model which includes an integration routine originally advanced by Gear* was developed and demonstrated to simulate, in principle, the chemical changes which may occur in the photooxidation of hydrocarbons, using as input data a set of elementary reactions, corresponding rate constants and appropriate starting conditions. Application of this model to the photooxidation of pottant and plastic materials used in the LSA module designs should provide for the first time a reliable predictive capability regarding the useful lifetime of these materials.

During the first quarter of this year the general mechanism of elementary reactions has been reviewed and improved. The earlier mechanism consisting of 46 reactions has been simplified considerably by reducing the number of formal termination steps since it became apparent that the major termination process goes via the peroxy radicals. Thus, we have eliminated all the other radical terminations and disproportionations, retaining only the following:

$$ROO\cdot + ROO\cdot \longrightarrow RO_4R \tag{1}$$

$$CROO\cdot + CROO\cdot \longrightarrow \text{Disproportionation (in cage)} \tag{2}$$

$$RO\cdot + RO\cdot \longrightarrow ROOR \text{ (crosslinking)} \tag{3}$$

$$R\cdot + R\cdot \longrightarrow RR \quad \text{"} \tag{4}$$

$$R\cdot + RO\cdot \longrightarrow ROR \tag{5}$$

In addition, we have included new reactions of oxygen with acyl radicals (from Norrish type I) to form peracids, which then decompose to form carbon dioxide:

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* C. W. Gear, Comm. ACM, 14, 176 (1971).

$$RCO\cdot + O_2 \longrightarrow RCOOO\cdot \quad (6)$$

$$RCOOO\cdot + RH \longrightarrow \text{Peracid} + R\cdot \quad (7)$$

$$\text{Peracid} \xrightarrow{h\nu} RCOO\cdot + OH\cdot \quad (8)$$

$$RCOO\cdot \longrightarrow R\cdot + CO_2 \quad (9)$$

We have also eliminated the sensitized decomposition of BOOH by energy transfer from excited ketones, and reduced the value of the rate constant for the sensitized decomposition of ROOH ($k = 10^8$). The photochemical reactions of small ketones formed by the Norrish type II process have also been added for completeness. The result is that we now have to deal with 36 reactions (down from 46) and 30 different species (down from 33).

Having changed the mechanism significantly, the integration parameters require manipulation to afford appropriate results on a realistic time-scale. We are now in the process of gaining hands-on experience of varying the integration parameters by feeding different input data to the computer. No dramatic differences have been observed to modify any of our earlier conclusions, namely that the major products predicted are ketones, alcohols and water with both scission by ketone cleavage and some crosslinking by radical recombination taking place (see Appendix).

The computer output shows the predicted concentration profiles of all the chemical species involved over time but the short time scale of days and hours implies more work on our model is necessary.

## 2. Photooxidation of Model Alkanes

We have continued to monitor the photooxidation of n-decane and 2,4-dimethyl pentane (DMP) initiated with peroxide and/or ketone as models for the photooxidation of polyethylene and ethylene segments of EVA in order to validate the general mechanism and computer product simulation.

The major products have been established earlier to be isomeric ketones, alcohols and water. To get clearer insight into the mechanism we have been doing finger-print analysis on the GC to identify the other products of photo-oxidation. This has proven to be an elusive exercise to date, but our efforts are continuing. We have also made preparation for LC analysis to attempt more effective and reproducible product separation. Some unavailable expected products are currently being synthesized for use as standards.

## 3. EVA Automated Viscometry

We have irradiated solutions of ELVAX in methylene chloride and measured the viscosity for different amounts of irradiation time in automated sequence. The neat ELVAX in solution shows a linear increase in viscosity with time of irradiation. This implies that the EVA crosslinks to some degree on irradiation (Figure 1).

Samples of additives used in the formulation to stabilize EVA have been supplied from Springborn Laboratories. We have also measured the viscosity changes in solutions of ELVAX containing up to 10% NAUGARD P (Uniroyal) or Cyasorb UV 531 (a substituted benzophenone from American Cyanamid). There is a similar linear increase in viscosity of these solutions showing the absence of any stabilization effect in solution.

The observation of increased viscosity, which strongly suggests that crosslinking is a major process, implies that there is a more likely possibility of the practical degradation of these materials deteriorating by shrinking and stripping from supports as the crosslinking takes place rather than the alternative embrittlement normally due to polymer scission and lower molecular weight.

We would now like to irradiate films of ELVAX with and without the additives and then measure the viscosities of the solutions formed by dissolving the irradiated films to measure the effectiveness of these stabilizers on EVA in the solid state.

Exposure of both clear and white EVA film samples to outdoor weathering conditions is being continued at EcoPlastics Limited. Some weatherometer experiments are also being planned.

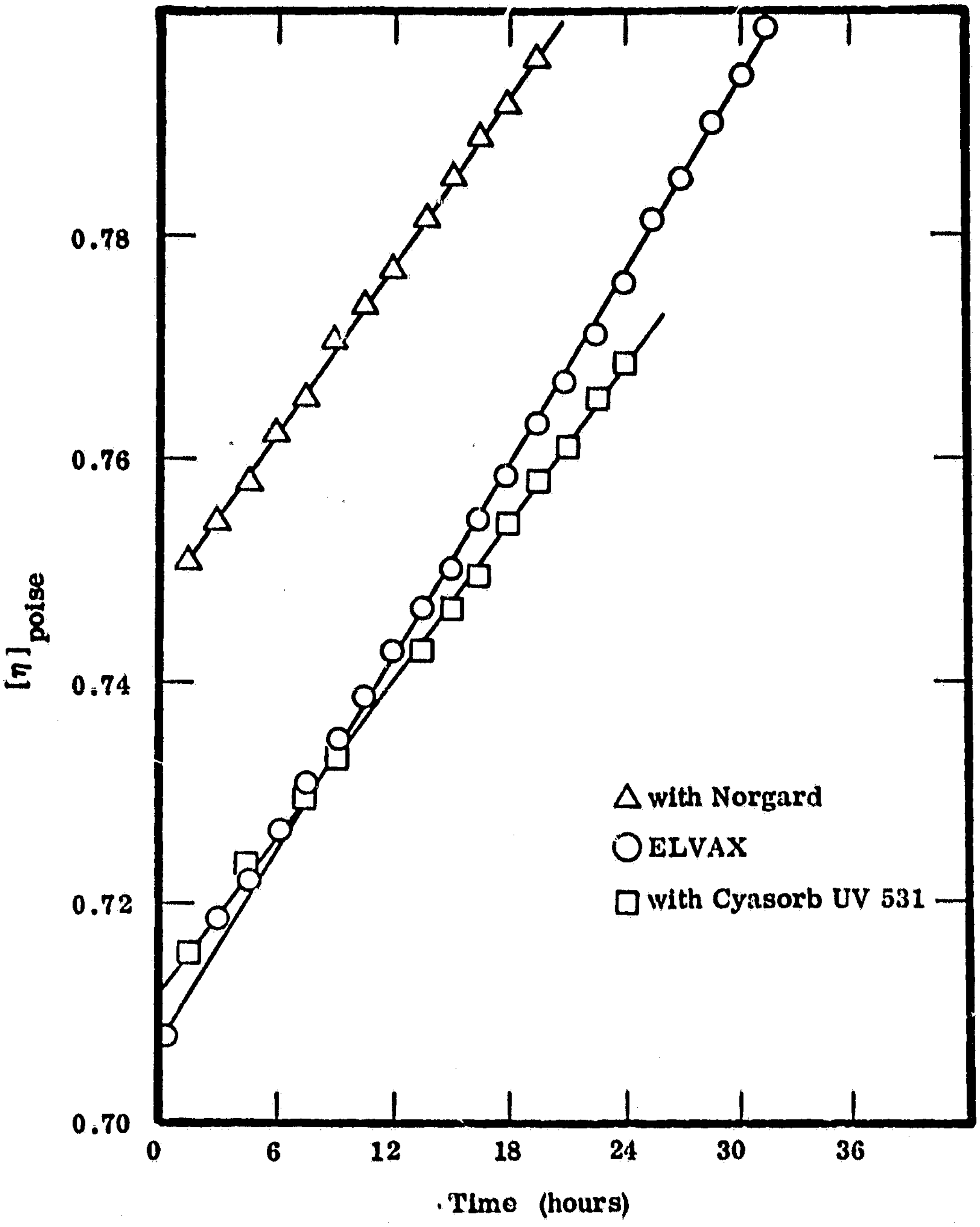

FIGURE 1. Intrinsic viscosity vs. irradiation time (ELVAX 0.47 g/100 ml $CH_2Cl_2$)

# Appendix

## Some Examples of Input-Output Data Used in the Current Simulation Routine for Alkane Photooxidation

```
                                     ***REACTION MATRIX***
                                     ---------------------

**********************************************************************************************

   1  I2                   OH        + RH          -> R           + HOH
   2  P2                   ROO       + RH          -> R           + ROOH
   3  P1                   R         + O2          -> ROO
   4  P4                   R         + ROOH        -> ROO         + RH
   5  P5                               ROOH        -> RO          + OH
   6  P6                   RO        + RH          -> ROH         + R
   7  P7                   ROO       + ROO         -> RO4R
   8  P8                   CROO      + CROO        -> CRO         + CRO         + SO2
   9  P9                               RO4R        -> CROO        + CROO
  10  P10                  CROO      + CROO        -> ROH         + KETONE      + SO2
  11  P11                              CRO         -> RO
  12  P12                  ROO       + ROO         -> ROH         + KETONE      + SO2
  13  P13                              RO          -> R           + KETONE
  14  P14                              KETONE      -> KET
  15  P141                             SMKETONE    -> KET
  16  P15                              KET         -> SMR         + RCO
  17  P151                 SMR       + RH          -> SMRH        + R
  18  P152                 RCO       + RH          -> ALDEHYDE    + R
  19  P153                             RCO         -> SMR         + CO
  20  P154                 RCO       + O2          -> RCOOO
  21  P155                 RCOOO     + RH          -> PERACID     + R
  22  P156                             PERACID     -> RCOO        + OH
  23  P157                             RCOO        -> R           + CO2
  24  P16                              KET         -> ALKENE      + SMKETONE
  25  P161                 KET       + O2          -> KETONE      + SO2
  26  P162                             KET         -> KETONE
  27  P163                             SO2         -> O2
  28  P18                  KET       + ROOH        -> KETONE      + RO          + OH
  29  P19                  CRO       + CRO         -> ROOR
  30  P20                              CROO        -> ROO
  31  P21                  SO2       + ALKENE      -> ROOH
  32  P22                  R         + ALKENE      -> BRANCH
  33  T3                   RO        + OH          -> ROOH
  34  T6                   RO        + RO          -> ROOR
  35  T7                   R         + R           -> RR
  36  T10                  R         + OR          -> ROR

**********************************************************************************************
```

```
                    ***INITIAL CONCENTRATION DATA (MOLES/L)***
                       ------------------------------------

**********VARIABLE SPECIES*********CONCENTRATION**********
*         ----------------         -------------         *
*                                                        *
*          1  OH                    0.0                  *
*          2  RH                    0.50000D+01          *
*          3  R                     0.10000D-03          *
*          4  HOH                   0.0                  *
*          5  ROO                   0.0                  *
*          6  ROOH                  0.0                  *
*          7  ROR                   0.0                  *
*          8  RO                    0.0                  *
*          9  ROH                   0.0                  *
*         10  RO4R                  0.0                  *
*         11  CROO                  0.0                  *
*         12  CRO                   0.0                  *
*         13  SO2                   0.0                  *
*         14  KETONE                0.0                  *
*         15  KET                   0.0                  *
*         16  SMKETONE              0.0                  *
*         17  SMR                   0.0                  *
*         18  RCO                   0.0                  *
*         19  SMRH                  0.0                  *
*         20  ALDEHYDE              0.0                  *
*         21  CO                    0.0                  *
*         22  RCOOO                 0.0                  *
*         23  PERACID               0.0                  *
*         24  RCOO                  0.0                  *
*         25  CO2                   0.0                  *
*         26  ALKENE                0.0                  *
*         27  ROOR                  0.0                  *
*         28  BRANCH                0.0                  *
*         29  RR                    0.0                  *
*         30  OR                    0.0                  *
*                                                        *
*********CONSTANT SPECIES*********CONCENTRATION**********
*         ----------------         -------------         *
*                                                        *
*         31  O2                    0.10000D-02          *
*                                                        *
**********************************************************
```

```
              ***REACTION RATE CONSTANTS...TEMP=300.0 K...***

     ***************************************************************************
     *
     *
     *     RXN LABEL        RATE CONSTANT        PRE-EXP FACTOR          E-ACT
     *     ---------        -------------        --------------          -----
     *
     *       1  T2          0.30000D+09
     *       2  P2          0.10000D+03
     *       3  P1          0.40000D+10
     *       4  P4          0.10000D+06
     *       5  P5          0.30000D-06
     *       6  P6          0.20000D+06
     *       7  P7          0.10000D+08
     *       8  P8          0.25000D+06
     *       9  P9          0.60000D+10
     *      10  P10         0.10000D+09
     *      11  P11         0.10000D+10
     *      12  P12         0.15000D+07
     *      13  P13         0.10000D+06
     *      14  P14         0.30000D-05
     *      15  P141        0.30000D-05
     *      16  P15         0.50000D+07
     *      17  P151        0.10000D+06
     *      18  P152        0.10000D+06
     *      19  P153        0.10000D+06
     *      20  P154        0.40000D+10
     *      21  P155        0.10000D+04
     *      22  P156        0.30000D-03
     *      23  P157        0.10000D+09
     *      24  P16         0.50000D+08
     *      25  P161        0.10000D+10
     *      26  P162        0.10000D+10
     *      27  P163        0.60000D+05
     *      28  P13         0.10000D+08
     *      29  P19         0.10000D+15
     *      30  P20         0.10000D+10
     *      31  P21         0.10000D+04
     *      32  P22         0.10000D+03
     *      33  T3          0.10000D+10
     *      34  T6          0.10000D+09
     *      35  T7          0.30000D+06
     *      36  T10         0.30000D+09
     *
     ***************************************************************************



     ***INTEGRATION REQUESTED--STARTING INTEGRATION PARAMETERS FOLLOW**

     **************************************************************************
     *                                               *
     *                                               *
     *                   ITEM                        *          VALUE
     *                   ----                        *          -----
     *                                               *
     *  INTEGRATION TIME LIMITS--STARTING TIME       *   0.0                    SEC
                                                     *
```

```
     ***INTEGRATION REQUESTED--STARTING INTEGRATION PARAMETERS FOLLOW**

   ***********************************************************************
   *                                          *
   *                                          *
   *               ITEM                       *          VALUE
   *               ----                       *          -----
   *                                          *
   *  INTEGRATION TIME LIMITS--STARTING TIME  *  0.0                SEC
   *                                          *
   *                                          *
   *                        --STOPPING TIME   *  0.50000000D+05     SEC
   *                                          *
   *                                          *
   *                                          *
   *  TIME STEP LENGTH--MINIMUM               *  0.10D-24   SEC
   *                                          *
   *                                          *
   *                 --INITIAL                *  0.10D-14   SEC
   *                                          *
   *                                          *
   *                                          *
   *  EQUAL TIME DATA STORAGE LIMIT           *        100  DATA SETS
   *                                          *
   *                                          *
   *                                          *
   *  MAXIMUM NUMBER OF INTEGRATION STEPS     *       1000  ITERATIONS
   *                                          *
   *                                          *
   *                                          *
   *  MAXIMUM CPU TIME LIMIT                  *        0.5  MIN
   *                                          *
   *                                          *
   *                                          *
   *  REQUESTED ERROR TOLERANCE               *  0.10D-04   PER STEP
   *                                          *
   *                                          *
   ***********************************************************************


   ***INTEGRATION MODE -- CHORD METHOD USING FULL ANALYTIC JACOBIAN AN,
                      -- GEAR STIFF METHODS EMPLOYED
```

```
                    *****FINAL CONCENTRATION ARRAY*****

    -->STARTING TIME
              TOTAL TIME=  0.0                SEC

    -->STOPPING TIME
              TOTAL TIME=  0.30202769D+02 SEC

    ****************************************************************************
    *     SPECIES        SPECIES        INITIAL CONC          FINAL CONC        *
    *      INDEX          LABEL            (M/L)                (M/L)           *
    *     -------        -------      ----------------     ---------------      *
    *
    *        1           OH             0.0                0.315706590D-18      *
    *
    *        2           RH             0.50000000D+01     0.49[illegible]220D+01      *
    *
    *        3           R              0.10000000D-03     0.236800610D-11      *
    *
    *        4           HOH            0.0                0.124273490D-07      *
    *
    *        5           ROO            0.0                0.189488800D-07      *
    *
    *        6           ROOH           0.0                0.157830087D-02      *
    *
    *        7           ROR            0.0                0.0                  *
    *
    *        8           RO             0.0                0.430491570D-15      *
    *
    *        9           ROH            0.0                0.500139050D-04      *
    *
    *       10           RO4R           0.0                0.598433330D-18      *
    *
    *       11           CROO           0.0                0.718120110D-17      *
    *
    *       12           CRO            0.0                0.257348250D-37      *
    *
    *       13           SO2            0.0                0.897887100D-14      *
    *
    *       14           KETONE         0.0                0.500035020D-04      *
    *
    *       15           KET            0.0                0.142053890D-18      *
    *
    *       16           SMKETONE       0.0                0.214297140D-09      *
    *
    *       17           SMR            0.0                0.145188795D-17      *
    *
    *       18           RCO            0.0                0.154411700D-18      *
    *
    *       19           SMRH           0.0                0.218965810D-10      *
    *
    *       20           ALDEHYDE       0.0                0.232885240D-11      *
    *
    *       21           CO             0.0                0.465898340D-12      *
    *
    *       22           RCOOO          0.0                0.123568360D-15      *
    *
    *       23           PERACID        0.0                0.185517060D-10      *
    *
    *       24           RCOO           0.0                0.556551090D-22      *
    *
    *       25           CO2            0.0                0.841041690D-13      *
    *
    *       26           ALKENE         0.0                0.214300840D-09      *
    *
    *       27           ROOR           0.0                0.430047270D-21      *
    *
    *       28           BRANCH         0.0                0.110301730D-17      *
    *
    *       29           RR             0.0                0.375200040D-09      *
    *
    *       30           OR             0.0                0.0                  *
    *
    *
    *
    ****************************************************************************
```

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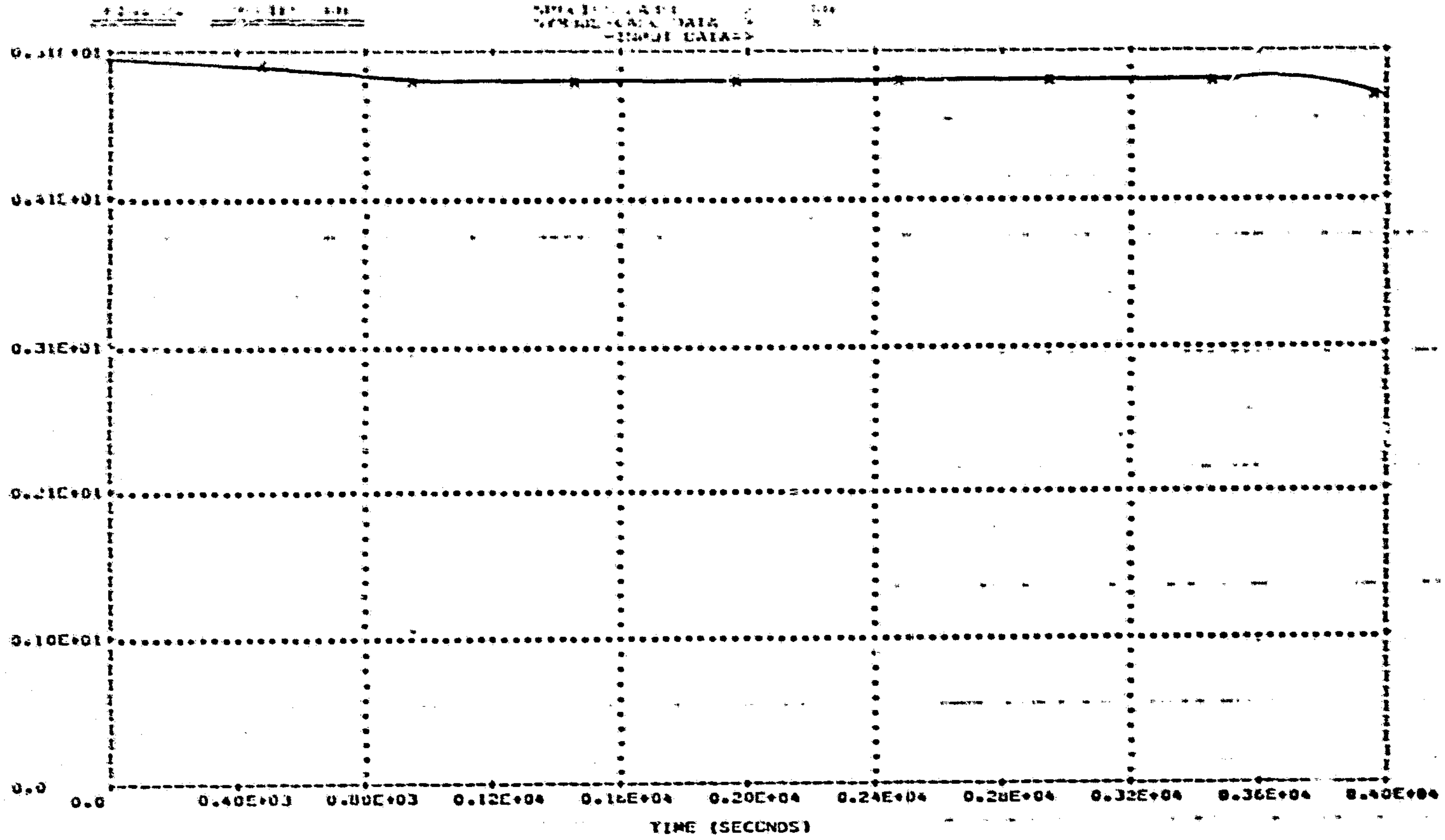

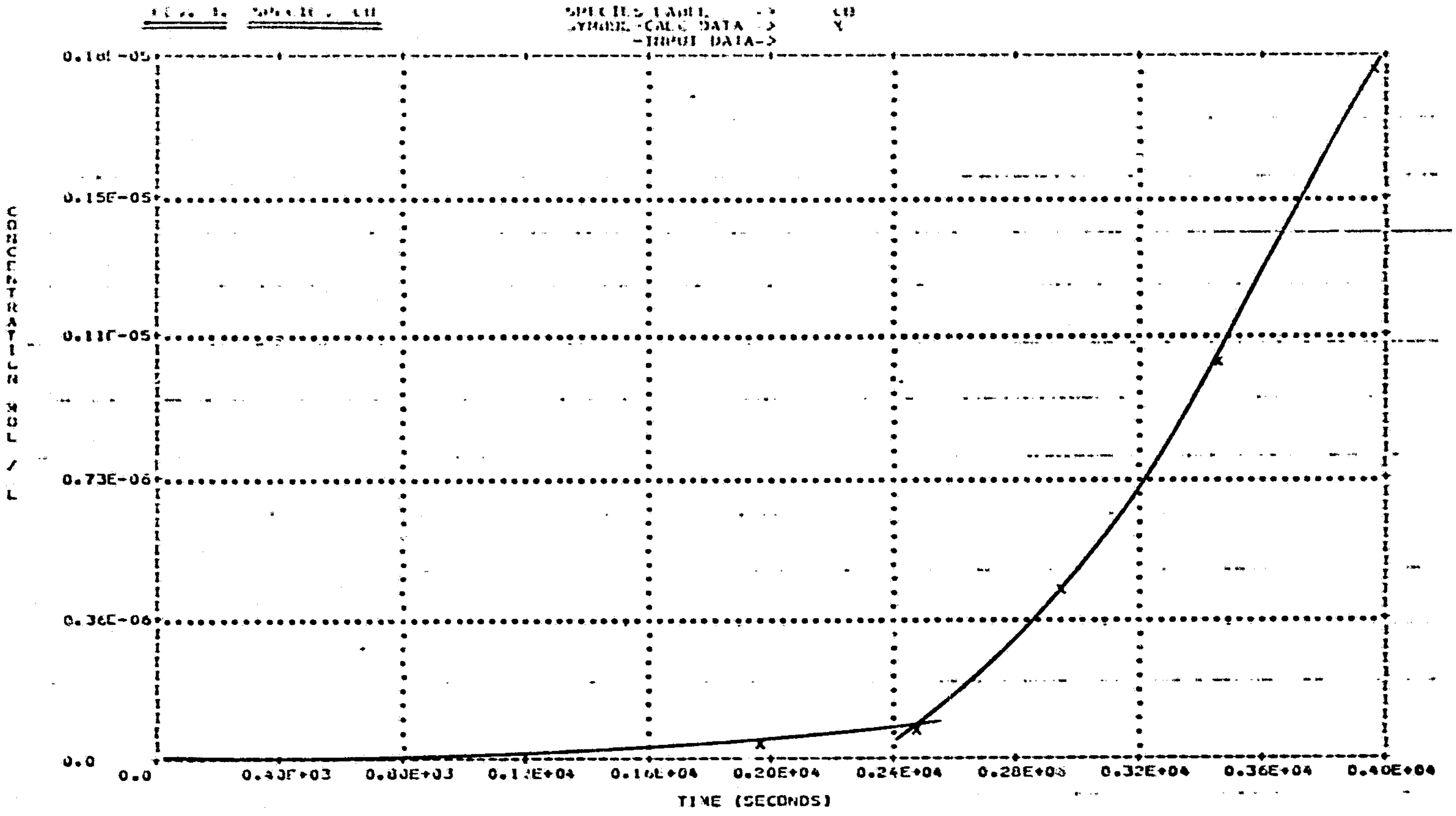

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FIG. 4. SPECIES ROOH

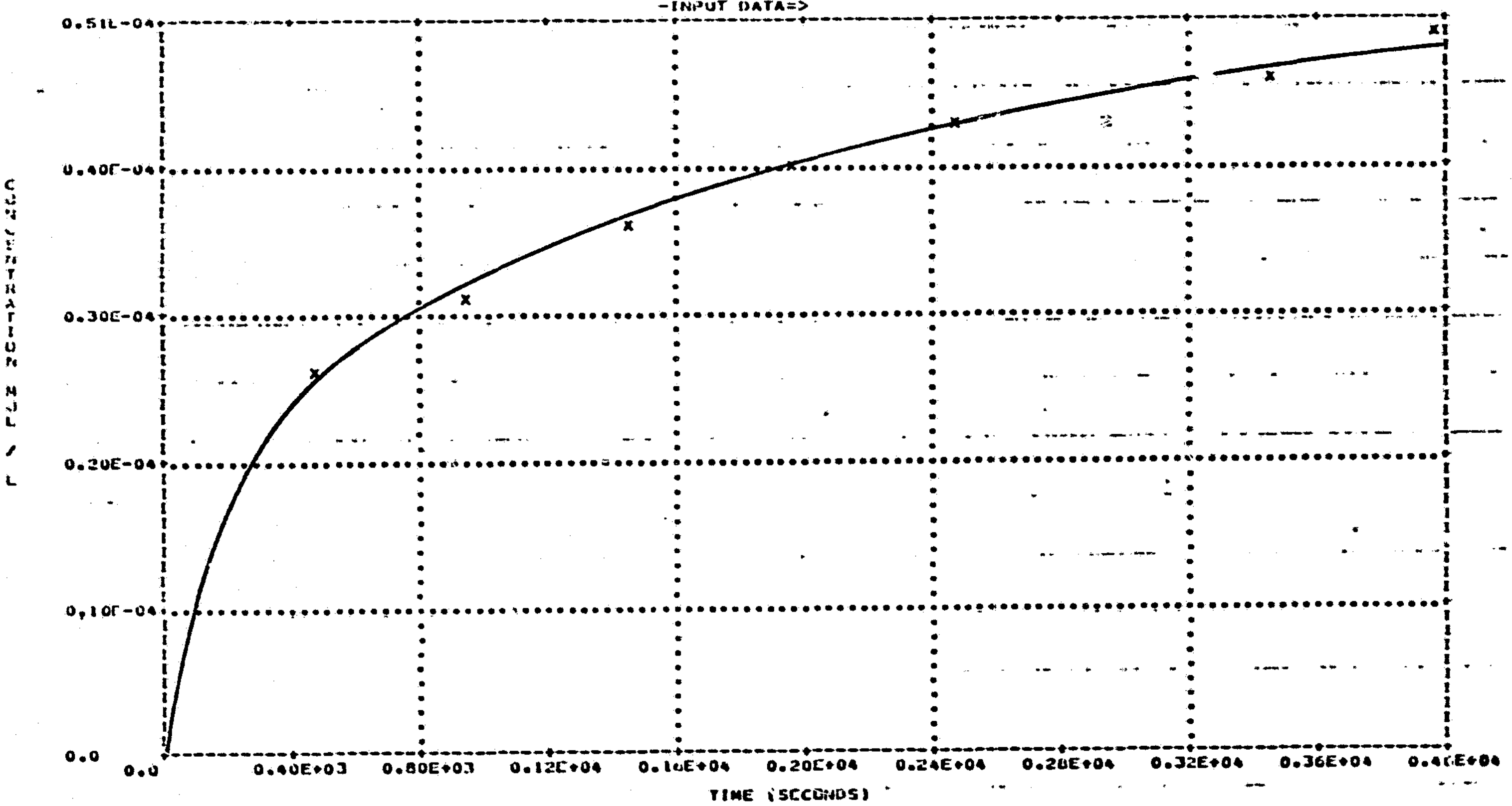

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FIG.10. SPECIES RCO

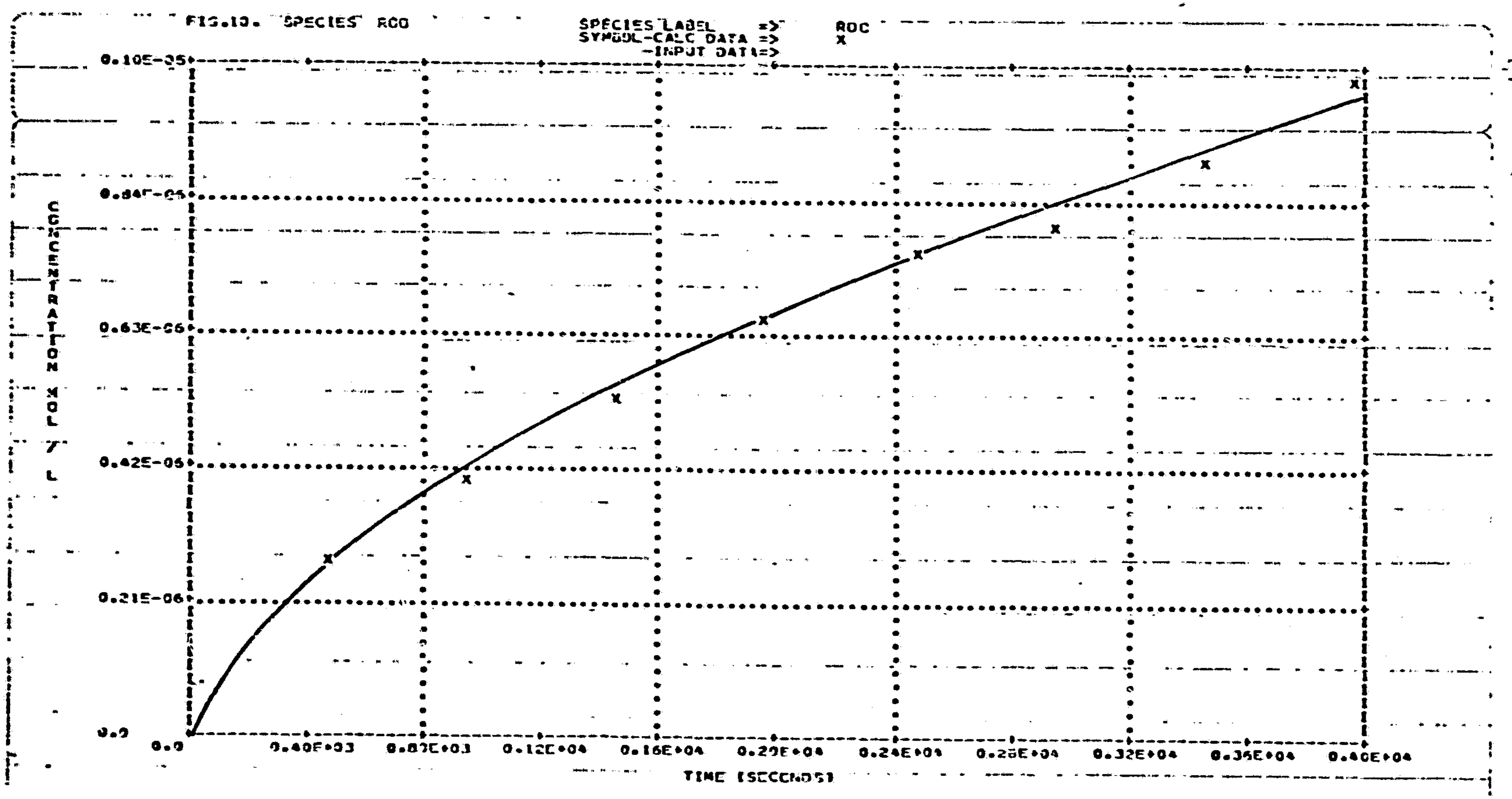
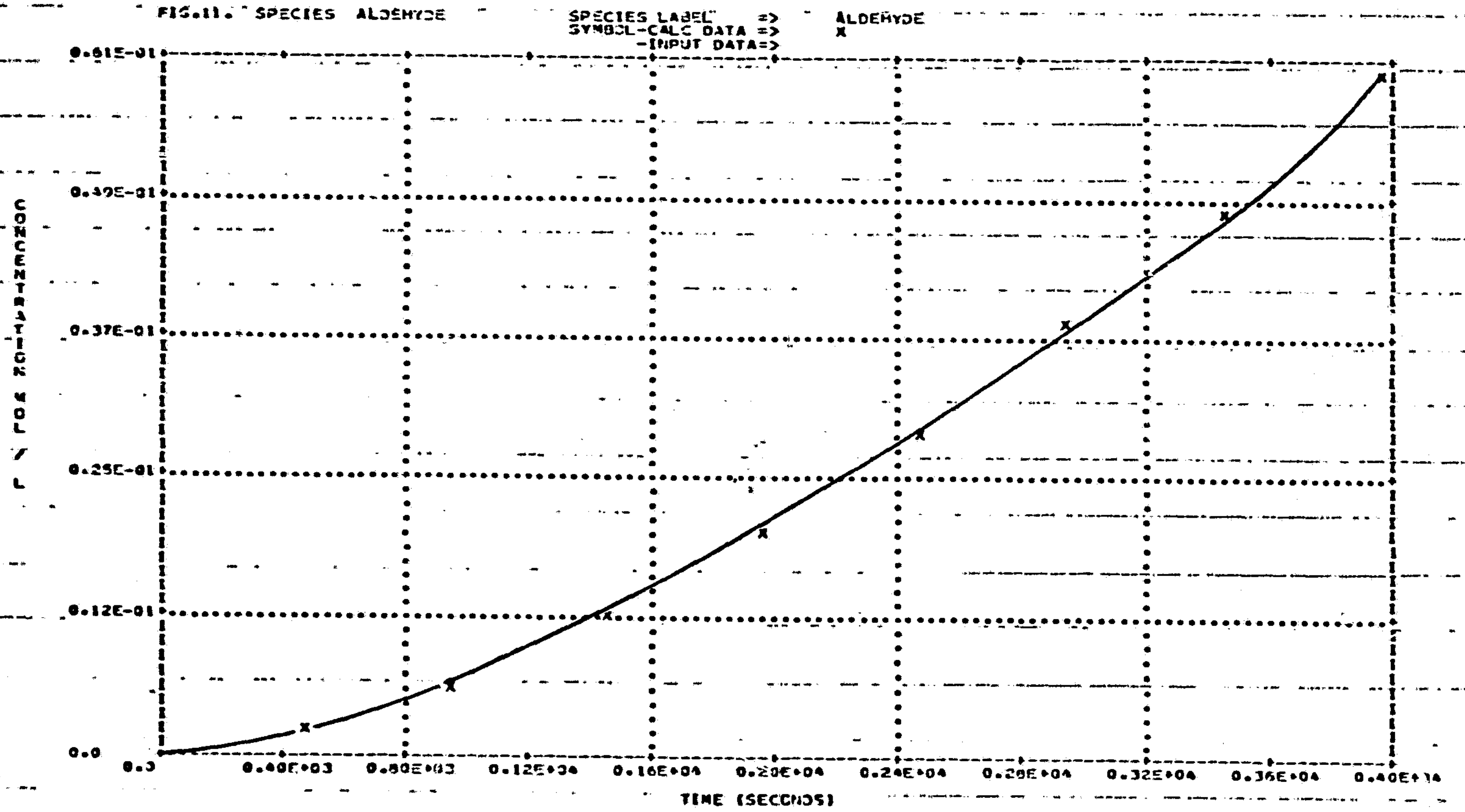


FIG.11. SPECIES ALDEHYDE



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