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MICROMOLECULAR MODELING

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- DEVELOP A REACTION KINETICS BASED MODEL OF THE PHOTODEGRADATION PROCESS EXPERIENCED BY ENCAPSULANTS

- DEVELOP A COMPUTER CAPABILITY TO UTILIZE THE REACTION KINETICS MODEL FOR PREDICTIVE PURPOSES

Goal

DEVELOP A REACTION KINETICS BASED MODEL OF THE PHOTODEGRADATION PROCESS EXPERIENCED BY ENCAPSULANTS, MEASURE ALL IMPORTANT RATE CONSTANTS, DEVELOP A COMPUTERIZED ~~PREDICTIVE~~ MODEL CAPABLE OF PREDICTION OF PHOTODEGRADATION RATE AND FAILURE MODES ASSOCIATED WITH IT OVER A THIRTY YEAR PERIOD, AND VALIDATE THE MODEL

FY84-85 Objectives

- EXTEND THE COMPUTERIZED DEGRADATION MODEL DEVELOPED FOR POLYETHYLENE TO EVA AND EVA (A-9918)
- EVALUATE THE EFFECT OF STABILIZERS ON PHOTODEGRADATION RATE
- PROVIDE GUIDELINES FOR SELECTION OF MOST EFFECTIVE CLASSES OF UV ~~ABSOR~~ STABILIZER
- INITIATE ~~THE~~ STUDY OF THE EFFECT OF TEMPERATURE VARIATION ON THE MODEL

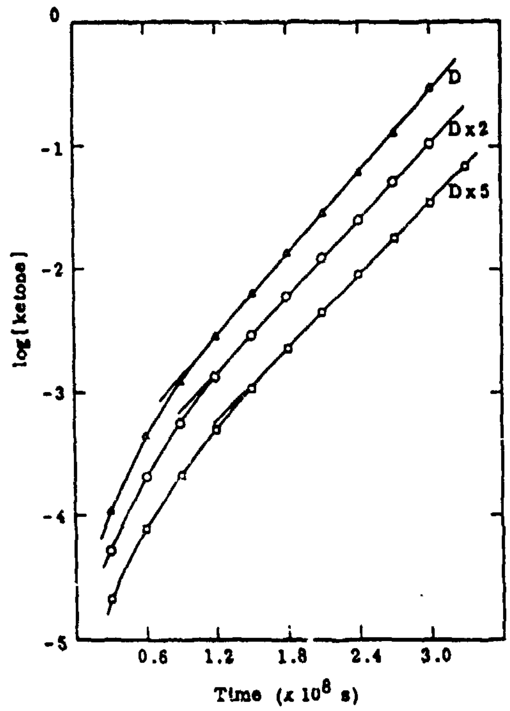
Accomplishments

- THE COMPUTERIZED PHOTODEGRADATION MODEL FOR POLYETHYLENE IS SHOWN TO CORRECTLY PREDICT FAILURE (EMBRITTLEMENT) OF ELVAX 150 ON OUTDOOR EXPOSURE, AND CROSS LINKED ELVAX 150 ON OUTDOOR EXPOSURE
- OUTDOOR EXPOSURE AND ACCELEROMETER TESTS INDICATE THAT CROSS-LINKING EVA DOES NOT SIGNIFICENTLY CHANGE ITS DEGRADATION RATE
- PARALLEL TESTS ON STABILIZED POLYETHYLENE AND EVA (A 9918) SHOW THAT THE EFFECT OF THE STABILIZER PACKAGE IS APPROXIMATELY EQUIVALENT ON BOTH POLYMERS — IE THE PE MODEL CAN BE USED FOR A-9918 WITH MINOR CHANGES, AND STABILIZER CONSUMPTION RATE IS A USEFUL DIAGNOSTIC MEASURE FOR EARLY PHOTODEGRADATION
- COMPUTERIZED MODEL INDICATES THAT PEROXIDE (HYDROPEROXIDE) DECOMPOSERS AND UV ABSORBERS ARE MOST EFFECTIVE STABILIZERS — BETTER THAN ANTIOXIDANTS
- EFFECT OF TEMPERATURE CYCLING IS BEING INVESTIGATED

Elementary Reactions in Polymer Photooxidation and Corresponding Rates

Reaction	Rate constant
RO_2 + RH → ROOH + RO_2	0.1×10^{-2}
RO_2 + RO_2 → ROH + Ketone + SO_2	0.1×10^{2}
RO_2 + ROH → ROOH + Ketone + HOO	0.5×10^{-1}
HOO + RH → HOOH + RO_2	0.5×10^{-2}
HOO + RO_2 → ROOH + SO_2	0.1×10^{8}
RO_2 + Ketone → ROOH + PeroxyCO	0.5×10^{-2}
RO_2 + ROOH → ROOH + Ketone + OH	0.5×10^{-1}
RO_2 + SMROH → ROOH + Aldehyde + HOO	0.5×10^{-2}
RO_2 + Aldehyde → ROOH + SMRCO	0.1×10^{3}
OH + RH → RO_2 + Water	0.3×10^{9}
Ketone → KET*	0.3×10^{-5}
SMKetone → KET*	0.3×10^{-5}
KET* → $SMRO_2$ + SMRCO	0.5×10^{7}
SMRCO → $SMRO_2$ + CO	0.5×10^{6}
KET* → Alkene + SMKetone	0.5×10^{8}
KET* + O_2 → Ketone + SO_2	0.1×10^{8}
KET* + ROOH → Ketone + RO + OH	0.1×10^{2}
KET* → Ketone	0.1×10^{10}
SO_2 → O_2	0.6 x 10
SO_2 + Alkene → ROOH	0.1×10^{4}
$SMRO_2$ + RH → SMROOH + RO_2	0.1×10^{-2}
SMROOH → SMRO + OH	0.3×10^{-4}
SMRO + RH → SMROH	0.1×10^{6}
SMRCO + O_2 → SMRCOOO	0.1×10^{8}
SMRCOOO + RH → SMRCOOOH + RO_2	0.1×10^{-1}
SMRCOOOH → $SMRCO_2$ + OH	0.1×10^{-8}
ROOH → RO + OH	0.3×10^{-4}
RO → $SMRO_2$ + Aldehyde	0.1×10^{6}
RO + RH → RO_2 + ROH	0.1×10^{6}
$SMRCO_2$ + RH → Acid + RO_2	0.1×10^{6}
RO_2 + RO_2 → ROOR	0.1×10^{-8}

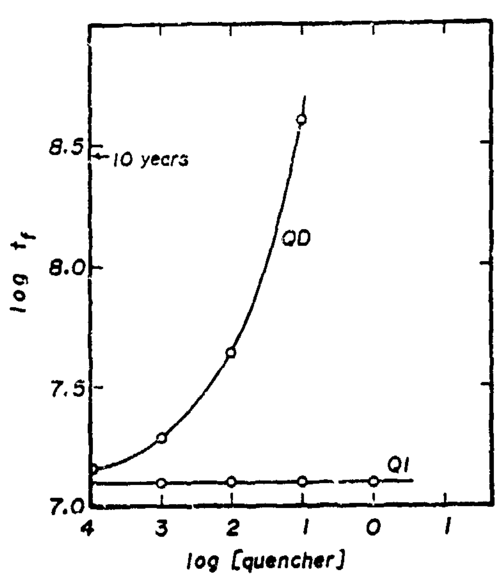
Effect of Termination Rate on Product Formation During Photooxidation



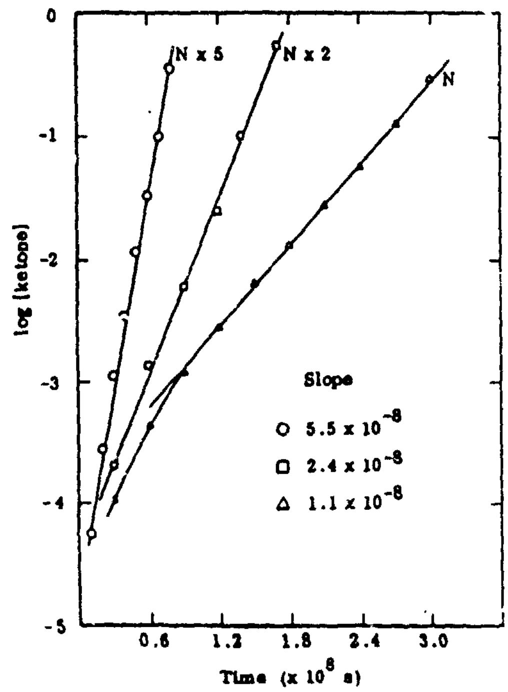
Stabilization of PE

$$ROOH + QD \xrightarrow{10^6} Products$$

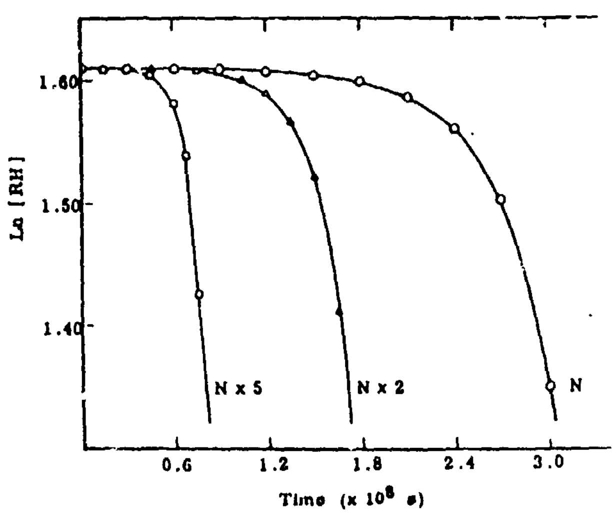
$$KET^* + Q1 \xrightarrow{10^6} Ketone + Heat$$



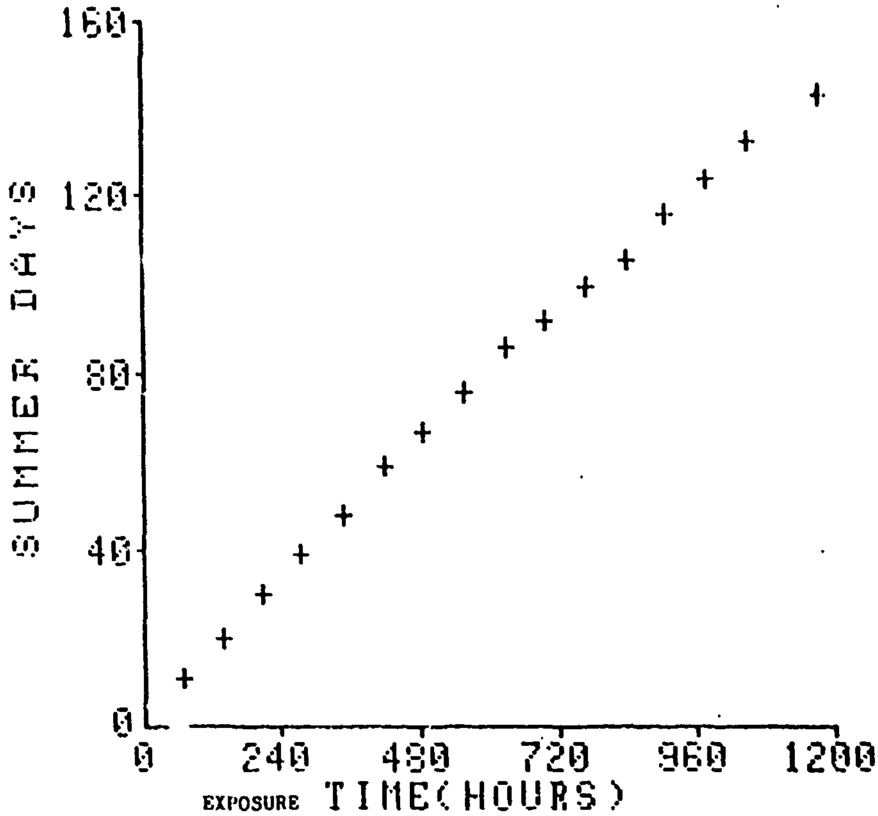
Effect of Intensity on Product Formation During Photooxidation



Photooxidation as a Function of Intensity of Light



Equivalent Solar Exposure (Summer Days) vs
Actual Accelerated Ager Exposure Time



Key Finding

THE COMPUTERIZED MODEL INDICATES THAT A COMBINATION OF A UV ABSORBER AND A HINDERED AMINE LIGHT STABILIZER (HALS) IS THE MOST EFFECTIVE STABILIZER SYSTEM