A COMPUTER SIMULATION OF RIGID POLYURETHANE FOAM FORMATION

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ABSTRACT

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By

P. V. S. R. Krishnam Raju

A computer simulation of polyurethane foam formation, based on available literature data, is presented in this work. The model describes the prepolymer, or 2-step, process for producing foam. A brief description of foam formation is presented and followed by the chemistry of selected model compounds. The kinetics of the model compounds are given in a mathematical form which is useful for modeling the actual reaction and heat transfer steps in the foaming process. A relation between extent of reaction, polymer chain length, and time of reaction is derived. A relation between the number average molecular weight and chain length is also derived. The kinetics of the cross-linking and foaming reactions are presented in a mathematical form. A heat balance is made on the system to determine the time necessary to evaporate the blowing agent and the adiabatic temperature rise in the system. A computer program was written based on all of the above mathematical equations. After the results are obtained a comparison between experimentally observed data and the computer simulation shows that the models are correct in their essential features. This is believed to be the first successful computer simulation of a 2-step polyurethane foam formation process which includes: (1) the prepolymer formation step, (2) the subsequent polymerization, crosslinking, and gel stages of the reaction; and (3) the heat transfer and blowing agent evaporation steps.

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P. V. S. R. Krishnam Raju

A THESIS

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To my family.

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INTRODUCTION

Unlike many other great discoveries in chemistry, polyurethanes are not the outgrowth of an accidental finding, but are the result of painstaking and systematic efforts to develop new polymers. Polyurethanes are among the most recent additions to the many commercially important classes of polymers. The term polyurethane is more one of convenience than of accuracy, since these polymers are not derived by polymerizing a monomeric urethane molecule, nor are they usually polymers containing primarily urethane groups. The polyurethanes include those polymers which contain a significant number of urethane groups regardless of what the chemical structure of the rest of the molecule may be.

The polyurethane foams in rigid types were developed during 1941-1945 by Bayer (3) and flexible types were reported first in 1952 by Hochtlen (14). The urethane foam industry developed first with diisocyanate-polyester combinations and more recently with diisocyanate-polyether combinations which are now used in largest volume. The polyester systems employed a 'One Shot' technique in which polyester, diisocyanate, foaming agent, catalysts and foam stabilizers are all mixed in one step, and permitted to foam. The first commercial use of polyethers employed a 'Pre Polymer' process, in which the polyether and diisocyanate were first reacted to form a prepolymer which was subsequently mixed with a catalyst, blowing agent, and stabilizers to produce foam. By the end of 1958, a one shot process for polyether foams was developed. This newer technology, and especially the very low foam density available from it, marked a further economic improvement in this industry.

At present the industrial technique of polyurethane foam formation is at an advanced stage. Unfortunately the details of the process are not very well described in the literature. This might be due to the heavy industrial competition in this field. Furthermore, partly due to the complexity of the process, a detailed mathematical analysis of the kinetics of the polymerization and foam formation is not available. This lack makes process analysis, trouble shooting, process scale-up, and plant design more of an art than a science.

The main goal of this work was to treat the kinetics and foam formation as a step-by-step process, so that the prepolymer, foaming and crosslinking reactions can be represented by mathematical equations. It was expected that the application of computer techniques to the mathematics of such a problem would prove fruitful, and that a computer simulation of the foaming process, in its entirety, would result.

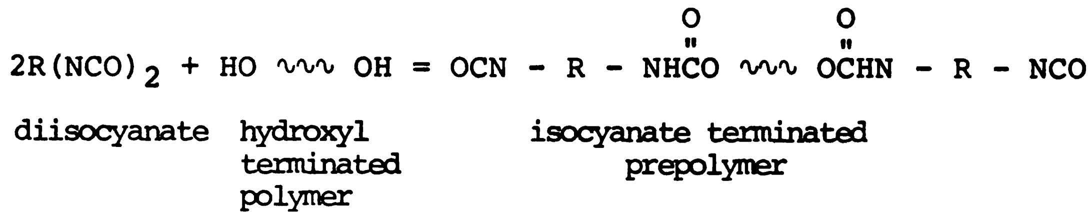
Because of the diverse types and large numbers of polyurethane foam formulations and processes in use, a general model was not developed. Instead a simulation was based upon a specific two step prepolymer process for producing polyurethane foam from tolylene diisocyanate and a diol using triethylene diamine as a catalyst and a Freon blowing agent. Variations in the reactant type, catalyst, or blowing agent may be incorporated in the program by appropriate modifications. The system chosen to model is of commercial importance. Some literature data for this system exists and makes possible comparison of the data with simulation predictions.

THEORY OF FOAM FORMATION

An understanding of the formation of rigid polyurethane foams involves consideration of the organic chemistry of the polymerization reactions leading to gas formation and molecular growth. In this section a brief description of foam formation along with the prepolymer step is presented. This is done in order that the reader can better understand and appreciate the organic chemistry and kinetics of the polymerization reactions which are presented in the next sections.

Two types of processes are generally used for producing rigid urethane foams. They are 'One Shot' and 'prepolymer' processes. The computer program of this work is based on the prepolymer process.

In the prepolymer process the reaction of isocyanate with hydroxyl terminated low molecular weight polymer is completed first. The amount of isocyanate present is in excess, so that when the reaction is completed, the prepolymer formed will contain only isocyanate end groups.



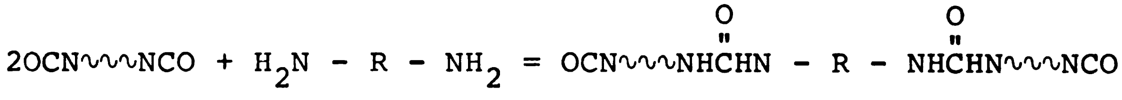
$$\underset{\text{diisocyanate}}{2R(NCO)_2} + \underset{\substack{\text{hydroxyl}\\ \text{terminated}\\ \text{polymer}}}{HO \sim\sim OH} = \underset{\substack{\text{isocyanate terminated}\\ \text{prepolymer}}}{OCN - R - NH\overset{O}{\overset{\|}{C}}O \sim\sim O\overset{O}{\overset{\|}{C}}HN - R - NCO} \qquad (A)$$

R - Alkyl or Aryl Group

This reaction is exothermic and is catalysed by amines and tin compounds.

The isocyanate terminated prepolymer is then foamed in further reaction using a catalyst, and crosslinking and blowing agents. In rigid urethane foams 'flurocarbon' is generally used as a blowing agent. The crosslinking reactions are exothermic, so the flurocarbon evaporates due to the heat liberated. In rigid urethane foams, the catalyst is chosen so that there is a balance between the exothermic crosslinking reactions and endothermic flurocarbon evaporation. The gas evolution and the polymer growth must be matched so that the gas is entrapped efficiently to produce a closed cell foam with good insulating properties and the resulting polymer has the right strength at the end of the gas evolution to maintain its volume without collapse or gross shrinkage.

In the model 'triethylene diamine' is used as a crosslinking agent. It has been experimentally shown that this substance acts both as a catalyst and a crosslinking agent (10,11). The isocyanate terminated polymer will react with triethylene diamine to form substituted urea. Flurocarbon and triethylene diamine are added to the prepolymer to start the foaming and crosslinking reactions.

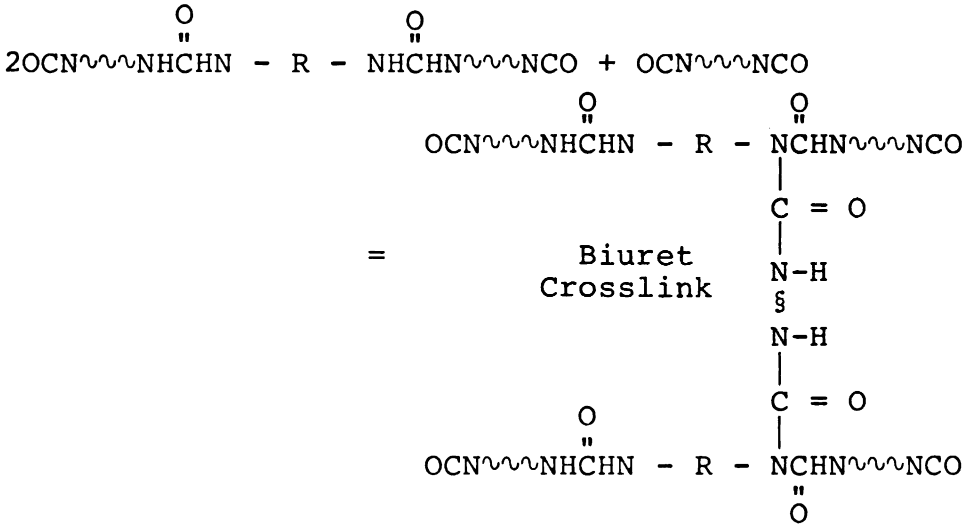


$$2OCN\sim\sim\sim NCO + H_2N - R - NH_2 = OCN\sim\sim\sim NH\overset{O}{\overset{\|}{C}}HN - R - NH\overset{O}{\overset{\|}{C}}HN\sim\sim\sim NCO$$

prepolymer diamine

(B)

The reaction is exothermic. It is also a chain extension reaction. Since the reactivity of the isocyanate group is high, even when it is part of a polymer chain, and the chain also contains active hydrogen atoms, crosslinking occurs with the virtual elimination of the isocyanate groups (6). The substituted urea will react with excess isocyanate to form a crosslink as indicated below (16).



$$2OCN\sim\sim\sim NH\overset{O}{\overset{\|}{C}}HN - R - NH\overset{O}{\overset{\|}{C}}HN\sim\sim\sim NCO + OCN\sim\sim\sim NCO$$

$$= \begin{array}{ll} & OCN\sim\sim\sim NH\overset{O}{\overset{\|}{C}}HN - R - N\overset{O}{\overset{\|}{C}}HN\sim\sim\sim NCO \\ & \qquad\qquad\qquad\qquad\qquad\qquad | \\ & \qquad\qquad\qquad\qquad\qquad\qquad C = O \\ & \qquad\qquad\qquad\qquad\qquad\qquad | \\ \text{Biuret Crosslink} & \qquad\qquad\qquad\qquad\qquad\qquad N-H \\ & \qquad\qquad\qquad\qquad\qquad\qquad \S \\ & \qquad\qquad\qquad\qquad\qquad\qquad N-H \\ & \qquad\qquad\qquad\qquad\qquad\qquad | \\ & \qquad\qquad\qquad\qquad\qquad\qquad C = O \\ & \qquad\qquad\qquad\qquad\qquad\qquad | \\ & OCN\sim\sim\sim NH\overset{O}{\overset{\|}{C}}HN - R - \underset{O}{\underset{\|}{N}}CHN\sim\sim\sim NCO \end{array}$$

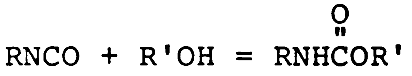
(C)

The crosslinking does not occur unless excess isocyanate is present. This is the main reason for using excess isocyanate in the prepolymer step.

CHEMISTRY OF FOAM FORMATION

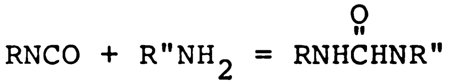
Urethane foam formation is the result of a series of rather complex chemical reactions leading to the formation of many chemical bonds other than the urethane groups. Instead of describing the exact reactions that take place during the foam formation, the reactions of model compounds are described in this section. This approach provides enough information to develop a kinetic model.

The reaction of an isocyanate with a hydroxyl compound produces urethane.



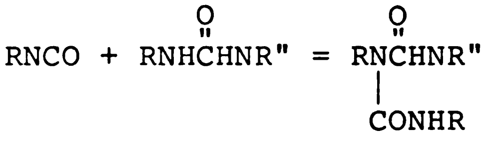
$$\mathrm{RNCO + R'OH = RNH\overset{\overset{O}{\|}}{C}OR'} \qquad (D)$$

Isocyanate also reacts with amine to form substituted urea.



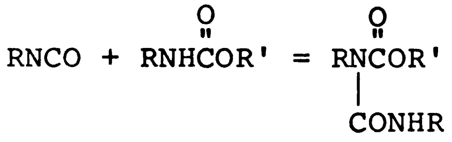
$$\mathrm{RNCO + R''NH_2 = RNH\overset{\overset{O}{\|}}{C}HNR''} \qquad (E)$$

Isocyanate also reacts with substituted urea and urethane to give a Biuret and Allophanate linkage, respectively.



$$\mathrm{RNCO + RNH\overset{\overset{O}{\|}}{C}HNR'' = R\underset{\underset{CONHR}{|}}{N}\overset{\overset{O}{\|}}{C}HNR''} \qquad (F)$$

Biuret



$$\mathrm{RNCO} + \mathrm{RNH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR'} = \mathrm{R}\underset{\mathrm{CONHR}}{\underset{|}{\mathrm{N}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR'} \qquad \text{(G)}$$

Allophanate

The last two reactions lead to branching and crosslinking. All the reactions described are exothermic. The reaction 'G' leading to the Allophanate formation is neglected in the model due to the fact that it is many times slower than the reaction 'F' which is considered to be slow by itself (16).

The relative rates of these isocyanate reactions in uncatalysed dilute systems is approximately one for reaction with urethane, to one hundred for a reaction with substituted urea, to about four hundred for a reaction with alcohol (16). The rates of these reactions are also influenced by the electronic structure of the reactants and steric hindrance.

One should bear in mind the possibility that relative rate data obtained in dilute solution may not be an accurate guide to rates in non-solvent systems, where the reaction medium changes markedly, as in foam formation. With these limits, however, the reactions of model compounds provide a starting point from which to build an understanding of urethane foam chemistry.

KINETICS

It was mentioned earlier that, in foam formation, one should ensure a proper balance between the exothermic crosslinking reactions and the endothermic flurocarbon evaporation. To obtain a computer simulation it is necessary to develop a thorough understanding of the kinetics of foam formation. The kinetics of the reaction of isocyanate with alcohol, amine, and urea are described separately. Next these kinetics are extended to describe the reactions of diisocyanate with diol, diamine, and diurea, the actual compounds in the foaming system.

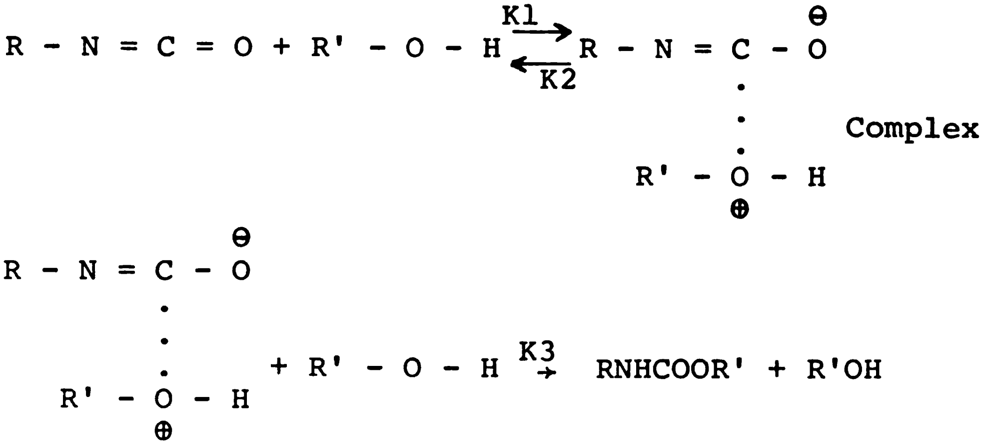
A. Reaction of Isocyanate With Alcohol

The mechanism and kinetics of the reaction of isocyanate with alcohol have been studied more thoroughly than those of any other isocyanate reactions. The first quantitative study of isocyanate, hydroxyl reaction was that of Davis and Farnum (8). A more detailed study of this reaction was reported by Baker and coworkers (2). The uncatalysed reaction between a monoisocyanate and alcohol is,

$$\mathrm{R - NCO + R'OH} \xrightarrow{\mathrm{Ko}} \mathrm{RNHCOOR'}$$

where Ko is the uncatalysed reaction rate constant.

The mechanism for the above reaction as proposed by Baker and Gaunt (2) is



$$R-N=C=O+R'-O-H \underset{K2}{\overset{K1}{\rightleftarrows}} \begin{array}{l} R-N=C-\overset{\ominus}{O} \\ \qquad\quad\;\; \vdots \\ \quad R'-\underset{\oplus}{O}-H \end{array} \quad \text{Complex}$$

$$\begin{array}{l} R-N=C-\overset{\ominus}{O} \\ \qquad\quad\;\; \vdots \\ \quad R'-\underset{\oplus}{O}-H \end{array} + R'-O-H \xrightarrow{K3} RNHCOOR' + R'OH$$

Here the alcohol acts as a catalyst in producing the complex. The rate of disappearance of isocyanate is given by

$$-\frac{d(NCO)}{dt} = K_1(NCO)(OH) - K_2\,(Complex)$$

where ( ) refers to the concentration of the particular component present in the parenthesis.

The rate of formation and disappearance of Complex is given by

$$\frac{d(Complex)}{dt} = K_1(NCO)(OH) - K_2(Complex) - K_3(OH)(Complex)$$

At steady state,

$$\frac{d(Complex)}{dt} = 0;\ \therefore\ (Complex) = \frac{K_1(NCO)(OH)}{(K_2+K_3(OH))}$$

For the entire reaction,

$$-\frac{d(NCO)}{dt} = \frac{d(urethane)}{dt} = Ko(NCO)(OH)$$

A slight manipulation gives the uncatalysed reaction rate constant as

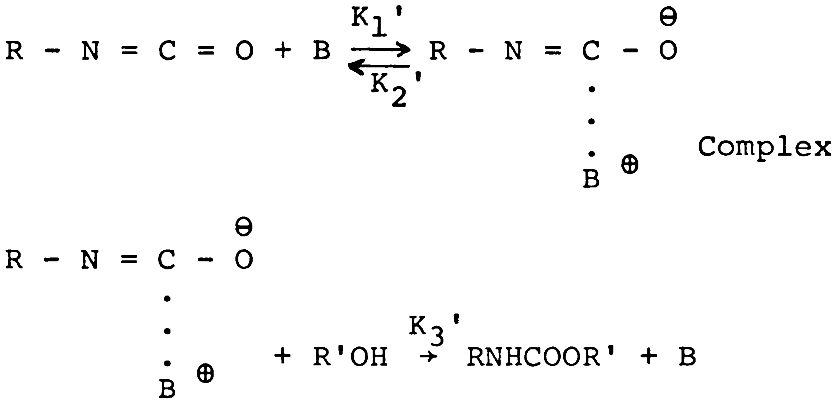
$$Ko = K_1K_3(OH)/(K_2 + K_3(OH))$$

The kinetics for the base catalysed reaction of isocyanate and alcohol are next considered.

$$RNCO + R'OH + B \xrightarrow{K} RNHCOOR' + B$$

where B is the catalyst.

The reaction mechanism proposed by Baker et al. (2) is,



$$R - N = C = O + B \underset{K_2'}{\overset{K_1'}{\rightleftarrows}} R - N = \underset{\substack{\vdots \\ B^{\oplus}}}{C} - \overset{\ominus}{O} \quad \text{Complex}$$

$$R - N = \underset{\substack{\vdots \\ B^{\oplus}}}{C} - \overset{\ominus}{O} + R'OH \xrightarrow{K_3'} RNHCOOR' + B$$

By the same type of mathematical treatment as done for uncatalysed reaction, the reaction rate constant for the catalysed reaction is obtained

$$K = K_1'K_3'(B)/(K_2' + K_3'(OH))$$

The experimentally observed rate constant for the catalysed reaction of isocyanate with alcohol is the sum of the rate constants for the uncatalysed and catalysed reactions.

$$K_{exp} = Ko + K$$
$$= K_1K_3(OH)/(K_2 + K_3(OH)) + K_1'K_3'(B)/(K_2' + K_3'(OH))$$

The catalytic function of alcohol raises doubt whether or not any reaction occurs by truly an uncatalysed mechanism. If the reaction is not catalysed by an external catalyst, it was experimentally shown that alcohol does act as a catalyst (9). However, in a catalysed system, the uncatalysed reaction rate constant is of a very small order of magnitude compared to the catalytic reaction rate constant. The overall reaction rate constant can therefore be simplified as

$$K_{exp} = Ku + Kc(B)$$

(If one assumes that the overall reaction rate constant is independent of hydroxyl concentration.)

where Ku is the uncatalysed reaction rate constant.

Kc is the catalytic coefficient for the particular catalyst.

The above assumption that the overall reaction rate constant is independent of hydroxyl concentration was verified by Baker and Holdsworth (2).

B. Reaction of Isocyanate With Amine

Systematic studies of the reaction of isocyanate with amine were carried out by Craven and Baker (2). Upon the basis of their observations they suggested the following mechanism.

1. Spontaneous Reaction:

$$ArNCO + ArNH_2 \underset{K_2}{\overset{K_1}{\rightleftarrows}} \text{Complex 1}$$

$$\text{Complex 1} + ArNH_2 \overset{K_3}{\rightarrow} \underset{\text{sub urea}}{(ArNH)_2CO} + ArNH_2$$

2. Product Catalysed Reaction:

$$\text{Complex 1} + (ArNH)_2\ CO \overset{K_3'}{\rightarrow} 2(ArNH)_2CO$$

Ar → alkyl or aryl radical, at steady state;

$$\frac{d(\text{Complex})}{dt} = 0$$

Then a slight mathematical manipulation gives,

$$Ka = K_1(K_3(NH_2) + K_3'(\text{sub urea}))/(K_2 + K_3(NH_2) + K_3'\ (\text{sub urea}))$$

where Ka is the overall rate constant for the isocyanate amine reaction.

For the initial stages of the reaction when the concentration of substituted urea is very small

$$Ka = K_1K_3(NH_2)/(K_2 + K_3(NH_2))$$

If K_2 is also small and can be neglected compared to $K_3(NH_2)$ then Ka can be assumed to be constant for the initial stages of the reaction.

For the final stages of the reaction when the concentration of the substituted urea is large compared to that of amine then,

$$Ka = K_1K_3'(\text{sub urea})/(K_2 + K_3'(\text{sub urea}))$$

Since K_2 is much smaller than K_3' (sub urea) then Ka can be assumed to be constant for the final stages of the reaction.

On the whole the rate constant for the amine, isocyanate reaction may be assumed to be constant for the entire reaction.

C. Reaction of Isocyanate With Ureas

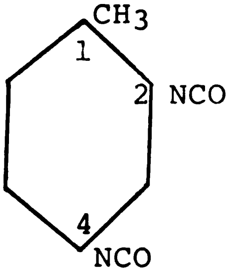
Because of the relatively high temperatures required and the many side reactions possible at these temperatures, the reaction between isocyanate and substituted urea is a difficult one to study kinetically with satisfactory results. Though the initial reaction leads to biuret, the active hydrogens in this compound are as active as those in the original substance, so many side reactions take place. Dissociation of biuret and other products may occur at higher temperatures. Kinetic data about this reaction are not available in the literature so the rate constant for this reaction is assumed to be constant for the entire reaction.

D. Reactions of Diisocyanate With Diol, Diamine and Diurea

The kinetics of these reaction have to be considered, since these are the main ingredients of the foaming system.

The reactions of diisocyanates with diol are more complicated kinetically than are those of monoisocyanates previously described. The initial reactivity of diisocyanate is similar to that of monoisocyanate substituted by an activating group, in this case a second isocyanate group. As soon as one isocyanate group has reacted with alcohol, the remaining isocyanate group has a reactivity similar to that of a monoisocyanate substituted by a urethane group. A urethane group in meta or para position has only a mild activating effect, much less than an isocyanate group in meta or para position. So the reactivity of a diisocyanate having both isocyanate groups on one aromatic ring should decrease significantly as the reaction passes approximately fifty percent completion.

An example illustrating these effects is 2, 4-tolylene diisocyanate.



The most reactive group should be the 4-position isocyanate, which is activated by 2-position isocyanate group. The 2-position group has similar activation initially by the 4-position group but compensating deactivation by the 1-position methyl group. After the 4-position isocyanate group has reacted with alcohol, the 2-position isocyanate group is even less reactive than initially because of strong deactivation by the 1-methyl group, far overshadowing the very slight activating tendency of the 4-position urethane group. This example was verified experimentally (15). The data from the experiments for the reaction of diisocyanates with n-butanol are:

Isocyanate Reactant	$K \times 10^2$	$K \times 10^3$
2,6-Tolylene Diisocyanate	1.5	2.46
2,4-Tolylene Diisocyanate	3.3	2.77

To illustrate the above-discussed material a computer program was written for the formation of uncatalysed urethane polymer from diisocyanate and diol. One program was run taking into consideration that the rate of reaction decreases significantly as the reaction crosses fifty percent completion. The results obtained are compared with another set of results on the same system but on the assumption that both isocyanate groups have equal reactivity throughout the entire reaction. The results from both the above cases are then compared with the values obtained experimentally by Bailey et al. (1), on the same system. All the results are tabulated in Appendix A.

From the table in Appendix A, one may conclude that the results obtained by taking into consideration the unequal reactivity of isocyanate groups are in close agreement with the experimental values.

The reactions of diisocyanate with diamine are considered next. Since in the foam formation, diamine is added to isocyanate terminated prepolymer, where the isocyanate groups are not on the same aromatic ring, but are far apart, both the isocyanate groups have equal reactivity toward diamine. Therefore the rate constant for this reaction is the same for both the isocyanate groups.

Similar reasoning applies to the reaction of diisocyanate with diurea, where the reaction rate constant is the same for both the isocyanate groups.

DEVELOPMENT OF FINAL MATHEMATICAL EQUATIONS

The kinetic expressions derived so far must be put in a mathematical form which allows solution with the computer. This section deals with the mathematical treatment of various expressions. Relations between extent of reaction and chain length and number average molecular weight and chain length are also derived for bifunctional monomers.

A. Mathematical Treatment of Prepolymer

The prepolymer reaction can be represented simply as:

$$\underset{(OH)}{\text{Diol}} + \underset{(NCO)}{\text{Diisocyanate}} \overset{Ko}{=} \text{Urethane}$$

In the development of the kinetics for the hydroxyl, isocyanate reaction it was concluded that the overall reaction rate constant is dependent only on the catalyst concentration. Therefore fixing the catalyst concentration fixes the overall reaction rate constant. The decrease in the reaction rate constant as the reaction crosses fifty percent completion will be taken into account in the computer program. Thus, the prepolymer step can be represented in mathematical form as:

$$\frac{d(NCO)}{dt} = -Ko(OH)(NCO) = \frac{d(OH)}{dt} \qquad (H)$$

Knowing Ko and initial concentrations of diol and diisocyanate the above equation can be solved on the computer using 'Eulers method.' The Eulers algorithm is of the form

$Yi = Y(xo) + h\ t(xo,Y(xo))$

Yi = new value of Y

$Y(xo)$ = old value of Y

h = step size

$t(xo,Y(xo))$ = derivative of Y with respect to x at the old value of Y

The algorithm is repeated for subsequent steps until Yi exceeds some desired upper limit. The smaller the step increment, the better are the results. The solution would give the change in reactant concentrations with respect to time. Then, from these, extent of reaction can be calculated with respect to time.

The extent of reaction is defined as the fraction of OH groups that have reacted at a particular time.

B. Molecular Weight of the Prepolymer

The molecular weight of the prepolymer is of prime concern from the practical viewpoint, for unless the polymer is of sufficiently high molecular weight, it will not have desirable strength characteristics. It is therefore important to consider the change in polymer molecular weight with reaction time.

The residue from each diol and diisocyanate (separately) in the polymer chain is termed as a structural unit. The repeating unit in the chain consists of one structural unit. The number average degree of polymerization Xn is defined as the average number of structural units per polymer chain. Thus Xn is simply given as the total number of monomer molecules initially present divided by the total number of molecules present at time 't'.

$$Xn = (M)o/(M)$$

The number average molecular weight Mn, defined as the total weight of a polymer sample divided by the total number of molecules in it, is given by

$$Mn = Mo\ Xn \qquad \text{(I)}$$

where Mo is the mean molecular weight of one structural unit. In order to determine Mn, Xn should be known. A relation between Xn and extent of reaction is derived below, for a reaction containing only bifunctional monomers.

For the polymerization of the bifunctional monomers HO∿∿∿OH and OCN∿∿∿NCO where OCN∿∿∿NCO is present in excess, the number of OH and NCO groups is given by NA and NB, respectively. NA and NB are equal to twice the number of HO∿∿∿OH and OCN∿∿∿NCO molecules, respectively. The stoichiometric imbalance 'r' of the two functional groups is given by r = NA/NB. The ratio 'r' is always defined so as to have a value equal to or less than unity, but never greater than unity. The total number of monomer molecules is given by

$$\frac{(NA + NB)}{2} = NA(1 + 1/r)/2$$

The extent of reaction 'p' is introduced here and defined as the fraction of OH groups which have reacted at a particular time. The fraction of NCO groups that have reacted is given by 'rp'. The fraction of unreacted OH and NCO groups is (1-p) and (1-rp), respectively. The total number of polymer chain ends is given by the sum of the total number of unreacted OH and NCO groups. Since each polymer chain has two chain ends, the total number of polymer molecules is one-half the total number of chain ends or

$$(NA(1 - p) + NB(1 - rp))/2$$

The number average degree of polymerization is the total number of HO∿∿∿OH and OCN∿∿∿NCO molecules initially present divided by the total number of polymer molecules.

$$\begin{aligned} Xn &= NA(1 + 1/r)/2/(NA(1 - p) + NB\ (1 - rp))/2 \\ &= (1 + r)/(1 + r - 2rp) \qquad \text{(J)} \end{aligned}$$

The extent of reaction 'p' may be calculated as a function of time and temperature from the previously discussed polymerization kinetics. At some critical chain length, or equivalently at some critical extent of reaction, chain branches in the system reach a concentration such that crosslinking and gel formation begins. This critical extent of reaction, 'Pc', marks the onset of the crosslinking stage of the process. Prepolymers are formed by reacting to extents of reaction of less than 'Pc'.

C. Mathematical Treatment of the Crosslinking Step

The crosslinking reactions taking place in the foam formation can be simplified as

$$\text{Isocyanate} + \text{Amine} \overset{K_1}{=} \text{Sub Urea}$$

$$\text{Isocyanate} + \text{Sub Urea} \overset{K_2}{=} \text{Biuret}$$

In the development of the kinetics of the above reactions it was concluded that the reaction rate constants for the various reactions can be assumed to be constant for the entire reaction. Also from the kinetics these equations can be mathematically represented as,

$$\frac{d(\text{NCO})}{dt} = -K_1(\text{NCO})(\text{amine}) - K_2(\text{sub urea})(\text{NCO}) \qquad (K)$$

$$\frac{d(\text{amine})}{dt} = -K_1(\text{NCO})(\text{amine}) \qquad (L)$$

$$\frac{d(\text{sub urea})}{dt} = K_1(\text{NCO})(\text{amine}) - K_2(\text{sub urea})(\text{NCO}) \qquad (M)$$

$$\frac{d(\text{biuret})}{dt} = K_2(\text{sub urea})(\text{NCO}) \qquad (N)$$

Knowing K_1, K_2, initial concentrations of diisocyanate and diamine, the equations can be solved on the computer using 'Eulers method.' The solution gives the rate of variation of the concentration of the reacting species with respect to time. The heat evolved during crosslinking is calculated by knowing the moles of sub urea and biuret formed, with respect to time. The amount of heat required to evaporate the flurocarbon can be calculated knowing the weight of the flurocarbon and its enthalpy of vaporization. The temperature rise in the system is obtained from a heat balance.

COMPUTER MODEL

The computer program was written for a 'prepolymer' process for producing rigid polyurethane foam, with the specific system comprised of (1) diol, (2) diisocyanate, (3) triethylene diamine, (4) flurocarbon. The reasons for selecting the particular system were mentioned earlier. The three variables in the computer program are (1) weight of diol, (2) weight of diamine, (3) required foam density. For a given foam density and given weight of diol and diamine, the computer program calculates the time required for prepolymer formation and the foam time.* From the results obtained one can judge whether the particular formulation is suitable for foaming or not.

The computer program is broadly divided into two parts, one describing the prepolymer step and the second describing the crosslinking and foaming reactions. The calculations for the prepolymer reaction are done in the following manner on the computer.

1. For a given weight of diol the equivalent amount of diisocyanate required is calculated. The calculated weight is then corrected for the specified NCO/OH ratio.

---

*Defined on page 29.

2. Concentrations of diol and diisocyanate are calculated and the ratio of initial concentrations is found.

3. The mathematical equation (H) representing the prepolymer formation is solved using Eulers method, with very small time increments.

4. From the heat balance, the maximum temperature increase in the mixture is obtained, assuming an adiabatic reaction system.

5. The kinetic chain length and number average molecular weight are determined using relations (J) and (I).

6. The change of reaction rate constant with temperature is taken into account using an Arrhenius equation, $K = A \exp (\Delta E/RT)$.

7. The decrease in the overall reaction rate constant is taken into account once the extent of reaction crosses fifty percent, (as discussed for tolylene diisacyante in the kinetic section).

The crosslinking reactions are solved on the computer in the following order:

1. Weight of amine is calculated from the percentage amine charged. The weight of surfactant is also calculated.

2. The weight of Freon required is calculated for a given density of foam, using the relation from the literature (4),

$$F = 28.21/D^{0.9}$$

where F = flurocarbon %

D = required foam density, lbs/cu. ft.

3. The concentration of amine and isocyanate in the foaming mixture is calculated.

4. The mathematical equations representing the crosslinking reactions (K,L,M,N) are solved on the computer by using Eulers method.

5. The amount of heat liberated is calculated from the amount of biuret and substituted urea formed.

6. The heat required for Freon to evaporate is obtained.

7. The temperature rise in the foam mixture is calculated under the assumption that there are no heat losses from the system.

8. The change of reaction rate constants with respect to temperature is taken into account using an Arrhenius equation.

The computer model was developed assuming that the following quantities are known; these are also the input parameters for the computer program:

1. Hydroxyl number of diol
2. Weight of diol
3. Density of diol
4. Molecular weight of diol

5. Percentage of isocyanate in 2,4-tolylene diisocyanate
6. Density of diisocyanate
7. Molecular weight of diisocyanate
8. Density of diamine
9. Density of substituted urea
10. Heat evolved during the formation of one mole of sub urea
11. Heat evolved during the formation of one mole of biuret
12. Heat of vaporization of Freon at its boiling point
13. Rate constant for diol-diisocyanate reaction
14. Rate constant for diisocyanate-diamine reaction
15. Rate constant for diisocyanate-diurea reaction
16. Required foam density
17. Mean molecular weight of a structural unit
18. Desired ratio of NCO/OH
19. Density of Freon
20. Required percentage of diamine
21. Specific heat of foaming mixture

For the simulation model all of these quantities were obtained from the literature. Typical values are in computer output in Appendix B.

The program is written in such a way that the heat liberated during the crosslinking reactions is initially utilised toward heating the foaming mixture, until the boiling point of Freon is reached. At the boiling point of Freon, the mixture remains at that temperature until all the

Freon has evaporated. This is the outcome of the assumption that there are no heat losses. In actual foaming operation, generally cooling is provided. In such a situation the heat removed could be simply added to the existing program.

The computer program along with its output for one particular run is attached in Appendix B.

DISCUSSION OF THE RESULTS

The computer program was tested for variations in required foam density and percentage of trirethylene diamine added for a given weight of diol. All the results are not presented here, but three of the results for different runs are given in Table 1.

In order to interpret the results given in Table 1, one must know the definitions of cream time and foam time. They are defined as follows:

Cream time: It is the time required for the solution to get supersaturated with the gaseous blowing agent.

Foam time: It is the time required for the foam to reach its maximum volume.

From the literature it is known (16) that for a rigid polyurethane foam, the cream time is approximately ten seconds and the foam time is approximately 60-120 seconds. The simulation provides reasonable estimates for the quantities as shown in the table. Most of the foam formulations used in industry contain a triol or a quadrol. These compounds give a highly crosslinked structure to the foam, compared with the diols. Since in the model only diols were used, there were no data available in the literature for this particular system, to compare the details of the results.

Table 1

Run	Foam Density lbs./cu. ft.	Percent Amine	Foam Time Seconds	Cream Time Seconds	Time for the Prepolymer to Reach 99.99% Completion; Seconds
1	1.5	3.0	75-90	2-3	37.7
2	1.7	2.0	300	10	66.5
3	1.9	1.0	..	45	138.6

The data obtained from one of the local firms (12) which manufacture rigid urethane foam by the prepolymer process, using flurocarbon as a blowing agent and diamine as a catalyst, are as follows:

Foam Density lbs/cu.ft.	Foam Time Seconds	Cream Time Seconds
1.5 to 1.6	80-85	2-3

These data agree very well with the results predicted by the computer program for that particular foam density. However, the amount of catalyst present in the industrial formulation was not known (12).

The results of the second computer run indicate that the particular foam formulation represented by the input data does foam, but it takes a very long time. To reduce the time necessary for foaming, the percentage of diamine would have to be increased.

The results of the third computer run indicate that the particular foam formulation does not attain the required foam density. The blank in the foam time means that the blowing agent did not evaporate completely. This is due to the fact that sufficient heat was not evolved to evaporate all the blowing agent. This indicates that not many cross-links were formed, which is the outcome of using less diamine.

The prepolymer step results are in agreement with the values available in the literature.

During the final stages of the crosslinking, when the chains start becoming stiffer the rate of collision of the molecules may be much slower than when the chains were free to move around. This was not taken into consideration in the model. This might result in a slightly longer time requirement for the crosslinking step than predicted by the program.

SUMMARY AND CONCLUSIONS

A plausible computer simulation of a 2-step, rigid polyurethane foam process was developed successfully. The results of the simulation appear to affirm the reliability of the essential features in the model. Polyurethane foam formation is the result of a series of rather complex chemical reactions, with simultaneous rapid changes in the temperature and viscosity of the medium. Predictions of the model are dependent on the accuracy of kinetic rate constants available, as the reaction medium changes. The rate constants that were used in the simulation were obtained from dilute solution literature data. These may not be a reliable guide, where the reaction medium changes markedly; however, they appear to give reasonable first estimates for the process simulations run.

With the availability of more accurate rate data, and the amounts of heat evolved during the various reactions, one would be in a better position to judge the model. However even now with the limited knowledge of the rate data, one could easily say that the model is predicting the results in the right direction, and in the right order of magnitude. The next step in developing the model would involve experimental studies aimed at providing some of the missing quantities mentioned above.

APPENDIX A

APPENDIX A

Time Hours	Experimental Values of Bailey et al.(1) Unreacted Diisocyanate %	Unequal Reactivity of Isocyanate Groups Unreacted Diisocyanate %	Equal Reactivity of Isocyanate Groups Unreacted Diisocyanate %
10	52.00	52.75	52.75
20	44.00	44.54	28.14
30	39.00	39.27	15.10
40	34.00	34.64	8.13
50	29.00	30.56	4.38
60	26.00	26.97	2.36

APPENDIX B

```
UNT VERSION OCT 73 A   17 16 12/09/74

                 PROGRAM URTHANE (INPUT,OUTPUT)
          C
          C...THIS PROGRAM TESTS THE MODEL FOR THE FORMATION OF PLOYURETHANE FOAMS
          C
    3            REAL  MWOH,MWNCO,KO,MWA,MO,K1,K2,MWPREPM
          C
          C....................READ IN VARIABLES...........................
          C
    3            READ 1,OHNO,PERNCO,WOH,MO,K1,K2,DOH,MWOH,DNCO,MWNCO,KO,MWA,HF,DA,
                1DS,HSUBU,H3,DENSITY,RATIO,DF,PA,SPHEAT
   63          1 FORMAT (7F10.4)
          C
          C....................PRINT INPUT VARIABLES.....................
          C
   63            PRINT 2,OHNO,WOH,DOH,MWOH,PERNCO,DNCO,MWNCO,DA,MWA
  111          2 FORMAT (1H1,50X,*INPUT VARIABLES*,
                1///,10X,*HYDROXYL NUMBER OF DIOL = *,27X,F15.6,
                2//,10X,*WEIGHT OF DIOL = *,39X,F15.6,*GRAMS*,
                3//,10X,*DENSITY OF DIOL = *,37X,F15.6,*GRAMS/LITER*,
                4//,10X,*MOLECULAR WEIGHT OF DIOL = *,28X,F15.6,
                5//,10X,*PERCENTAGE OF ISOCYNATE = *,27X,F15.6,*PERCENT*,
                6//,10X,*DENSITY OF ISOCYNATE = *,32X,F15.6,*GRAMS/LITER*,
                7//,10X,*MOLECULAR WEIGHT OF ISOCYNATE = *,22X,F15.6,
                8//,10X,*DENSITY OF AMINE = *,36X,F15.6,*GRAMS/LITER*,
                9//,10X,*MOLECULAR WEIGHT OF AMINE = *,26X,F15.6)
  111            PRINT 30,DS,HSUBU,H3,HF,KO
  127         30 FORMAT (//,10X,*DENSITY OF SUBSTITUTED UREA = *,25X,F15.6,*GRAMS/
                1LITER*,
                2//,10X,*HEAT EVOLVED BY THE FORMATION OF ONE MOLE OF SUBUREA = *,
                3F13.6,*KCAL*,
                4//,10X,*HEAT EVOLVED FOR ONE MOLE OF BIURET FORMED = *,8X,F15.6,
                5*KCAL*,
                6//,10X,*HEAT OF VAPORISATION OF FREON = *,19X,F15.6,*KCAL*,
                7//,10X,*RATE CONSTANT FOR OH NCO REACTION = *,15X,F15.6,*L/MOLE.
                8SEC.*)
  127            PRINT 40,K1,K2,DENSITY,MO,RATIO,DF,PA,SPHEAT
  153         40 FORMAT (//,10X,*RATE CONSTANT FOR NCO NH2 REACTION = *14X,F15.6,
                1*L/MOLE.SEC.*,
                2//,10X,*RATE CONSTANT FOR NCO SUBUREA REACTION = *,10X,F15.6,*L/
                3MOLE.SEC.*,
                4//,10X,*REQUIRED FOAM DENSITY = *,28X,F15.6,*LBS/CU.FT.*,
                5//,10X,*MEAN MOLECULAR WEIGHT OF TWO STRUCTURAL UNITS = *,7X,F15.6
                6,//,10X,*RATIO OF NCO/OH = *,34X,F15.6,
                7//,10X,*DENSITY OF FREON = *,36X,F15.6, *LBS/CU.FT.*,
                8//,10X,*PERCENT AMINE = *,36X,F15.6,*PERCENT*,
                9//,10X,*SPECFIC HEAT OF FOAMING MIXTURE = *,17X,F15.6,*CAL/M.C.*)
          C
          C......EQUIVALENT WEIGHTS OF DIOL AND ISOCYANATE.........
          C
  153            EWOH=56.1*1000./OHNO
  156            EWNCO= 42.*100./PERNCO
          C
          C.....THE WEIGHT OF ISOCYANATE REQUIRED FOR A GIVEN WEIGHT OF DIOL......
          C
  160            TWNCO=(WOH/EWOH)*EWNCO
          C
          C...........TOTAL WEIGHT OF ISOCYANATE REQUIRED................
          C
  164            WNCO=TWNCO*RATIO
  166            TWEIGHT=WOH+WNCO
          C
          C.................VOLUMES OF DIOL AND ISOCYANATE...............
          C
  170            VOH=WOH/DOH
  172            VNCO=WNCO/DNCO
  174            VOL=VOH+VNCO
          C
          C........INTIAL CONCENTRATIONS OF DIOL AND ISOCYANATE........
          C
  176            COOH=WOH/(MWOH*VOL)*2.0
  202            CONCO=WNCO/(MWNCO*VOL)*2.0
          C
          C.............RATIO OF INTIAL CONCENTRATIONS.........
          C
  205            RICONC=COOH/CONCO
```

```
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   207        PRINT 3,WOH,WNCO,COOH,CONCO,RICONC
   224      3 FORMAT (/////(50X,* PREPOLYMER INPUT VARIABLES *,
             1//,10X,*WEIGHT OF DIOL = *,25X,E15.8,*GRAMS*,
             2//,10X,*WEIGHT OF ISOCYNATE = *,19X,E15.6,*GRAMS*,
             3//,10X,*INITIAL CONCENTRATION OF OH = *,13X,E15.8,*MOLES/LITER*,
             4//,10X,*INITIAL CONCENTRATION OF NCO = *,12X,E15.8,*MOLES/LITER*,
             5//,10X,*RATIO OF INITIAL CONCENTRATIONS OF OH TO NCO = *,E15.8)
        C
        C............STORE INTIAL CONCENTRATIONS............
        C
   224        COH=COOH
   226        CNCO=CONCO
        C
        C .................CALCULATIONS FOR THE FORMATION OF PREPOLYMER........
        C
   227        PRINT  301
   233    301 FORMAT (1H1,56X,*PREPOLYMER FORMATION REACTIONS*)
   233        PRINT 200
   237    200 FORMAT (    //,7X,*TIME*,13X,*DOHDT*,13X,*DNCODT*,14X,*CNCO*,15X,
             1*COH*,12X,*EXTREAC*,17X,*XN*)
   237        PRINT 201
   243    201 FORMAT (/,5X,*SECONDS*,7X,*MOLES/LITER.SEC.*,4X,*MOLES/LITER.SEC.*
             1, 4X,*MOLES/LITER*, 8X,*MOLES/LITER*)
        C
        C...........INTIALIZING VARIABLES..............
        C
   243        TIME=0
   244        T1=0.0
   245        HU=25.0
   247        HEATEV=0.0
   250        ITOTAL=42000
   251        IEVERY=100
   253        IK=ITOTAL/IEVERY
   256        DO 21 J=1,IK
   260        DO 4 I=1,IEVERY
        C
        C...........EULERS METHOD...............
        C
   261        DT=0.01
   262        DOHDT=-KO*COH*CNCO
   265        DNCODT=-KO*COH*CNCO
   267        COH=COH+DOHDT*DT
   272        CNCO=CNCO+DNCODT*DT
   275        DUDT=KO*COH*CNCO
        C
        C.................HEAT EVOLVED DURING POLYMERIZATION.........
        C
   277        HEATEV=HEATEV+(DUDT*HU*DT*VOL)
        C
        C.......TEMPERATURE OF PREPOLYMER MIXTURE............
        C
   304        T1=(HEATEV*1000.0/(TWEIGHT*0.5))
   312        TEMP=T1+20.0
   314        TIME=TIME+DT
        C
        C..........EXTENT OF REACTION..............
        C
   316        EXTREAC=1.0-(COH/COOH)
        C
        C............CHAIN LENGTH...............
        C
   322        XN=(1.+RICONC)/(1.+RICONC-2.*RICONC*EXTREAC)
        C
        C....REDUCTION OF REACTION RATE CONSTANT AFTER 50 PERCENT OF REACTION...
        C
   332        IF(EXTREAC.GE.0.5) KO=0.0895
        C
        C.....CHANGE OF REACTION RATE CONSTANT WITH TEMPERATURE......
        C
   335        EC=EXP((11500.0/1.9872)*((1.0/297.0)-(1.0/(TEMP+273.0))))
   354        KO=KO*EC
   355        IF(EXTREAC.GE.0.9999) GO TO 29
   360      4 CONTINUE
   363     21 PRINT 5,TIME,DOHDT,DNCODT,CNCO,COH,EXTREAC,XN
   407      5 FORMAT (/,7(E18.6))
   407        GO TO 53
```

```
RUNT VERSION OCT 73 A   17 16 12/09/74
   407         29 PRINT35,TIME,DOHDT,DNCODT,CNCO,COH,EXTREAC,XN
   431         35 FORMAT (/,7(E18.6))
   431         53 CONTINUE
            C
            C....................MOLECULAR WEIGHT OF PREPOLYMER......................
            C
   431            MWPREPM=MO*XN
   433            PRINT 8,MWPREPM,TEMP
   443          8 FORMAT(////,5X,*NUMBER AVERAGE MOLECULAR WEIGHT OF PREPOLYMER = *,
                 1F12.4,10X,*FINAL TEMPERATURE OF PREPOLYMER = *,F5.2)
            C
            C........WEIGHT OF AMINE...........
            C
   443            PA=PA/100.0
   445            AMINE=TWEIGHT*PA/(1.-PA)
            C
            C......WEIGHT OF SURFACTANT.........
            C
   451            SURFACT=0.01*WOH
            C
            C...THE WEIGHT OF FLUROCARBON REQUIRED FOR A GIVEN DENSITY OF FOAM......
            C
   453            PRSENTF=28.21/(DENSITY)**0.90
   460            PRSENTF=PRSENTF/100.
   462            WF=PRSENTF*TWEIGHT/(1-PRSENTF)
            C
            C...................VOLUME AND WEIGHT OF FOAM MIXTURE.....................
            C
   466            VA=AMINE/DA
   470            VS=SURFACT/DS
   472            VF=WF/DF
   474            VFOAMMX=VOH+VNCO+VA+VS+VF
   501            WFOAMMX=TWEIGHT+WF+AMINE+SURFACT
            C
            C......CONCENTRATION OF ISOCYANATE IN THE END GROUPS OF PREPOLYMER......
            C
   505            ECNCO=((COOH*EXTREAC)+CONCO*(1.0-(RICONC*EXTREAC)))/2.0
            C
            C...CONCENTRATION OF AMINE AND ISOCYANATE IN FOAM MIXTURE......
            C
   520            FMXCNCO=(ECNCO+CNCO)*VOL/VFOAMMX
   524            CA=AMINE/(MWA*VFOAMMX)*2.0
   530            CNCO=FMXCNCO
   532            PRINT 13,CNCO,CA,WF
   543         13 FORMAT (1H1,45X,* FOAMING REACTION INPUT VARIABLES *,
                 1///,10X,*INITIAL CONCENTRATION OF ISOCYNATE IN FOAMING MIXTURE = *
                 2,E15.8,*MOLES/LITER*,
                 3//,10X,*INITIAL CONCENTRATION OF AMINE IN FOAMING MIXTURE = *,4X,
                 4E15.8,*MOLES/LITER*,
                 5//,10X,*WEIGHT OF FLOUROCARBON IN FOAMING MIXTURE = *,12X,E15.8,
                 6*GRAMS*)
            C
            C......CALCULATIONS FOR THE FOAMING AND CROSSLINKING REACTIONS..........
            C
   543            CAO=CA
   545            PRINT 302
   550        302 FORMAT (////,55X,*CROSSLINKING REACTIONS*)
   550            PRINT 300
   554        300 FORMAT (/////,4X,*TIME*,6X,*DNCODT*,6X,*DADT*,6X,*DSUBUDT*,5X
                 1,*DBDT*,8X,*CNCO*,7X,*CA*,7X,*CSUBU*,8X,*CB*,7X,*HEVOLD*,5X,
                 2HREQFTE*,6X,*TEMP*)
   554            PRINT 303
   560        303 FORMAT (/,2X,*SECONDS*,5X,*MOLES/*,5X,*MOLES/*,5X,*MOLES/*,5X,
                 1*MOLES/*,3X,*MOLES/LIT.*,1X,*MOLES/LIT.*,1X,*MOLES/LIT.*,1X,
                 2*MOLES/LIT.*,4X,*KCAL*,8X,*KCAL*,8X,*DEG C*)
   560            PRINT 304
   564        304 FORMAT (13X,*LIT/SEC.*,3X,*LIT/SEC.*,3X,*LIT/SEC.*,3X,*LIT/SEC.*)
            C
            C............INTIALIZING VARIABLES.,.............
            C
   564            CSUBU=0.0
   565            CB=0.0
   566            TIME=0.0
   567            HEVOLVD=0.0
   570            I2TOTAL=50
   572            I2EVERY=10
```

```
RUNT VERSION OCT 73 A    17 16 12/09/74
   573        58 I2K=I2TOTAL/I2EVERY
   577           DO 22 K=1,I2K
   601           DO 12 I=1,I2EVERY
              C
              C........EULEPS METHOD.........
              C
   602           DT =0.1
   603           DNCODT=-K1*CNCO*CA-K2*CNCO*CSUBU
   611           DADT=-K1*CNCO*CA
   613           DSUBUDT=K1*CNCO*CA-K2*CSUBU*CNCO
   617           DBDT=K2*CNCO*CSUBU
   621           CNCO=CNCO+DNCODT*DT
   624           CA=CA+DADT*DT
   627           CSUBU=CSUBU+DSUBUDT*DT
   632           CB=CB+DBDT*DT
   635           IF(DSUBUDT.LE.0.0) GO TO 900
              C
              C............HEAT EVOLVED DURING CROSSLINKING REACTIONS.......
              C
   637           HEVOLVD=HEVOLVD+(DSUBUDT*HSUBU+DBDT*HB)*VFOAMMX*DT
   647           GO TO 901
   650       900 HEVOLVD=HEVOLVD+(DBDT*HB*VFOAMMX*DT)
   656       901 CONTINUE
   656           TIME = TIME+DT
              C
              C.......TEMPERATURE OF THE FOAMING MIXTURE......
              C
   660           FTEMP=(HEVOLVD*1000.0)/(WFOAMMX*SPHEAT)
   666           TTEMP=FTEMP+20.0
              C
              C........HEAT REQUIRED FOR THE FLUROCARBON TO EVAPORATE ..............
              C
   670           HREQFTE=WF*HF
              C
              C...ASSUMPTION THAT TEMPERATURE DOES NOT RAISE WHEN FREON IS EVAPORATING
              C
   672           IF (TTEMP.GE.23.77) GO TO 43
   675           TEMP=TTEMP
   677           GO TO 66
   677        43 IF (HEVOLVD-HREQFTE) 44,45,46
   702        44 TEMP=23.77
   704           GO TO 66
   704        45 TEMP=23.77
   706           GO TO 66
   706        46 STEMP=(HEVOLVD-HREQFTE)*1000.0/(WFOAMMX*SPHEAT)
   715           TEMP=STEMP+23.77
              C
              C.....CHANGE OF REACTION RATE CONSTANT WITH TEMPERATURE......
              C
   717        66 EC=EXP((11500.0/1.9872)*((1.0/293.0)-(1.0/(TEMP+273.0))))
   736           K1=0.150
   737           K2=0.015
   741           K1=K1*EC
   743           K2=K2*EC
   744           SCA=CA0*0.0002
   746        12 CONTINUE
   751        22 PRINT 100,TIME,DNCODT,DADT,DSUBUDT,DBDT,CNCO,CA,CSUBU,CB,HEVOLVD,
                1HREQFTE,TEMP
  1007       100 FORMAT (/,12(E11.3))
              C
              C..........COUNTERS FOR PRINT STATEMENTS..........
              C
  1007           IF (I2TOTAL.EQ.50) GO TO 55
  1011           IF (I2TOTAL.EQ.100) GO TO 56
  1014           IF (I2TOTAL.EQ.1050) GO TO 57
  1017           GO TO 25
  1020        55 I2TOTAL=100
  1022           I2EVERY=50
  1023           GO TO 58
  1024        56 I2TOTAL=1050
  1026           I2EVERY=150
  1027           GO TO 58
  1030        57 I2TOTAL=9000
  1032           I2EVERY=600
  1033           GO TO 58
  1034        25 CONTINUE
                 END
```

Computer Output

```
                                              INPUT VARIABLES

HYDROXYL NUMBER OF DIOL =                                     57.000000
WEIGHT OF DIOL =                                              10000.000000GRAMS
DENSITY OF DIOL =                                             1090.000000GRAMS/LITER
MOLECULAR WEIGHT OF DIOL =                                    1900.000000
PERCENTAGE OF ISOCYNATE =                                     37.000000PERCENT
DENSITY OF ISOCYNATE =                                        1270.000000GRAMS/LITER
MOLECULAR WEIGHT OF ISOCYNATE =                               174.000000
DENSITY OF AMINE =                                            1000.000000GRAMS/LITER
MOLECULAR WEIGHT OF AMINE =                                   116.000000

DENSITY OF SUBSTITUTED UREA =                                 1000.000000GRAMS/ LITER
HEAT EVOLVED BY THE FORMATION OF ONE MOLE OF SUBUREA =        20.000000KCAL
HEAT EVOLVED FOR ONE MOLE OF BIURET FORMED =                  15.000000KCAL
HEAT OF VAPORISATION OF FREON =                               .043500KCAL
RATE CONSTANT FOR OH NCO REACTION =                           .447500L/MOLE.  SEC.

RATE CONSTANT FOR NCO NH2 REACTION =                          .150000L/MOLE.SEC.
RATE CONSTANT FOR NCO SUBUREA REACTION =                      .015000L/  MOLE.SEC.
REQUIRED FOAM DENSITY =                                       1.500000LBS/CU.FT.
MEAN MOLECULAR WEIGHT OF TWO STRUCTURAL UNITS =               1037.000000
RATIO OF NCO/OH =                                             1.020000
DENSITY OF FREON =                                            1480.000000LBS/CU.FT.
PERCENT AMINE =                                               3.000000PERCENT
SPECFIC HEAT OF FOAMING MIXTURE =                             .600000CAL/M.C.


                                             PREPOLYMER INPUT VARIABLES
WEIGHT OF DIOL =                                1.00000000E+04GRAMS
WEIGHT OF ISOCYNATE =                           1.176413E+03GRAMS
INITIAL CONCENTRATION OF OH =                   1.04214539E+00MOLES/LITER
INITIAL CONCENTRATION OF NCO =                  1.33872815E+00MOLES/LITER
RATIO OF INITIAL CONCENTRATIONS OF OH TO NCO =  7.78459306E-01
```

PREPOLYMER FORMATION REACTIONS

```
    TIME           DOHDT             DNCODT              CNCO             COH            EXTREAC            XN
  SECONDS    MOLES/LITER.SEC.   MOLES/LITER.SEC.    MOLES/LITER      MOLES/LITER
 1.000000E+00   -9.147270E-02     -9.147270E-02     7.145910E-01     4.180033E-01     5.988964E-01     2.102132E+00
 2.000000E+00   -7.753747E-02     -7.753747E-02     6.300424E-01     3.334596E-01     6.800258E-01     2.471062E+00
 3.000000E+00   -6.330737E-02     -6.330737E-02     5.597472E-01     2.631644E-01     7.474782E-01     2.893231E+00
 4.000000E+00   -5.039179E-02     -5.039179E-02     5.031148E-01     2.065320E-01     8.018203E-01     3.355012E+00
 5.000000E+00   -3.952530E-02     -3.952530E-02     4.583922E-01     1.618094E-01     8.447343E-01     3.838871E+00
 6.000000E+00   -3.079256E-02     -3.079256E-02     4.234474E-01     1.268647E-01     8.782659E-01     4.326406E+00
 7.000000E+00   -2.395011E-02     -2.395011E-02     3.962538E-01     9.967106E-02     9.043597E-01     4.800875E+00
 8.000000E+00   -1.865307E-02     -1.865307E-02     3.750930E-01     7.851020E-02     9.246648E-01     5.248803E+00
 9.000000E+00   -1.456868E-02     -1.456868E-02     3.585910E-01     6.200822E-02     9.404995E-01     5.660671E+00
 1.000000E+01   -1.141733E-02     -1.141733E-02     3.456814E-01     4.909865E-02     9.528369E-01     6.030886E+00
 1.100000E+01   -8.978483E-03     -8.978483E-03     3.355473E-01     3.896458E-02     9.626112E-01     6.357270E+00
 1.200000E+01   -7.083315E-03     -7.083315E-03     3.275654E-01     3.098259E-02     9.702704E-01     6.640321E+00
 1.300000E+01   -5.604191E-03     -5.604191E-03     3.212592E-01     2.467648E-02     9.763215E-01     6.882416E+00
 1.400000E+01   -4.444924E-03     -4.444924E-03     3.162638E-01     1.968103E-02     9.811149E-01     7.087097E+00
 1.500000E+01   -3.532869E-03     -3.532869E-03     3.122975E-01     1.571477E-02     9.849208E-01     7.258489E+00
 1.600000E+01   -2.812893E-03     -2.812893E-03     3.091423E-01     1.255957E-02     9.879484E-01     7.400869E+00
 1.700000E+01   -2.242902E-03     -2.242902E-03     3.066283E-01     1.004554E-02     9.903607E-01     7.518377E+00
 1.800000E+01   -1.790551E-03     -1.790551E-03     3.046225E-01     8.039741E-03     9.922854E-01     7.614842E+00
 1.900000E+01   -1.430829E-03     -1.430829E-03     3.030204E-01     6.437694E-03     9.938227E-01     7.693686E+00
 2.000000E+01   -1.144286E-03     -1.144286E-03     3.017397E-01     5.156966E-03     9.950516E-01     7.757899E+00
 2.100000E+01   -9.157190E-04     -9.157190E-04     3.007152E-01     4.132336E-03     9.960347E-01     7.810046E+00
 2.200000E+01   -7.331909E-04     -7.331909E-04     2.998950E-01     3.312264E-03     9.968217E-01     7.852296E+00
 2.300000E+01   -5.872941E-04     -5.872941E-04     2.992382E-01     2.655467E-03     9.974519E-01     7.886463E+00
 2.400000E+01   -4.705898E-04     -4.705898E-04     2.987120E-01     2.129275E-03     9.979568E-01     7.914051E+00
 2.500000E+01   -3.771802E-04     -3.771802E-04     2.982903E-01     1.707586E-03     9.983615E-01     7.936300E+00
 2.600000E+01   -3.023789E-04     -3.023789E-04     2.979523E-01     1.369563E-03     9.986858E-01     7.954225E+00
 2.700000E+01   -2.424552E-04     -2.424552E-04     2.976813E-01     1.098551E-03     9.989459E-01     7.968655E+00
 2.800000E+01   -1.944348E-04     -1.944348E-04     2.974640E-01     8.812310E-04     9.991544E-01     7.980264E+00
 2.900000E+01   -1.559432E-04     -1.559432E-04     2.972897E-01     7.059429E-04     9.993216E-01     7.989598E+00
 3.000000E+01   -1.250833E-04     -1.250833E-04     2.971499E-01     5.671515E-04     9.994558E-01     7.997101E+00
 3.100000E+01   -1.003377E-04     -1.003377E-04     2.970378E-01     4.550195E-04     9.995634E-01     8.003130E+00
 3.200000E+01   -8.049249E-05     -8.049249E-05     2.969478E-01     3.650681E-04     9.996497E-01     8.007973E+00
 3.300000E+01   -6.457543E-05     -6.457543E-05     2.968757E-01     2.929060E-04     9.997189E-01     8.011862E+00
 3.400000E+01   -5.180789E-05     -5.180789E-05     2.968178E-01     2.350125E-04     9.997745E-01     8.014985E+00
 3.500000E+01   -4.156598E-05     -4.156598E-05     2.967713E-01     1.985647E-04     9.998191E-01     8.017492E+00
 3.600000E+01   -3.334962E-05     -3.334962E-05     2.967341E-01     1.512987E-04     9.998548E-01     8.019505E+00
 3.700000E+01   -2.675793E-05     -2.675793E-05     2.967042E-01     1.213938E-04     9.998835E-01     8.021120E+00
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                                   FOAMING REACTION INPUT VARIABLES

         INITIAL CONCENTRATION OF ISOCYNATE IN FOAMING MIXTURE =  7.87835089E-01MOLES/LITER
         INITIAL CONCENTRATION OF AMINE IN FOAMING MIXTURE =      4.81184520E-01MOLES/LITER
         WEIGHT OF FLOUROCARBON IN FOAMING MIXTURE =              2.72198471E+03GRAMS

                                           CROSSLINKING REACTIONS

   TIME      DNCODT      DADT     DSUBUDT      D3DT       CNCO        CA        CSU3U        CB       HEVOLD     HREQFTE       TEMP
 SECONDS     MOLES/     MOLES/     MOLES/     MOLES/   MOLES/LIT. MOLES/LIT. MOLES/LIT. MOLES/LIT.    KCAL        KCAL        DEG C
            LIT/SEC.   LIT/SEC.   LIT/SEC.   LIT/SEC.
1.000E+00 -5.318E-02 -5.258E-02  5.199E-02  5.998E-04  7.328E-01  4.264E-01  5.444E-02  3.013E-04  1.354E+01  1.184E+02  2.157E+01
2.000E+00 -4.881E-02 -4.757E-02  4.634E-02  1.231E-03  6.820E-01  3.766E-01  1.033E-01  1.252E-03  2.593E+01  1.184E+02  2.300E+01
3.000E+00 -4.325E-02 -4.149E-02  3.973E-02  1.757E-03  6.359E-01  3.320E-01  1.464E-01  2.795E-03  3.678E+01  1.184E+02  2.377E+01
4.000E+00 -3.654E-02 -3.447E-02  3.241E-02  2.067E-03  5.965E-01  2.945E-01  1.819E-01  4.733E-03  4.594E+01  1.184E+02  2.377E+01
5.000E+00 -3.131E-02 -2.903E-02  2.676E-02  2.274E-03  5.629E-01  2.632E-01  2.111E-01  6.920E-03  5.357E+01  1.184E+02  2.377E+01
1.000E+01 -1.679E-02 -1.420E-02  1.150E-02  2.596E-03  4.492E-01  1.619E-01  2.998E-01  1.944E-02  7.788E+01  1.184E+02  2.377E+01
1.500E+01 -1.060E-02 -8.087E-03  5.572E-03  2.515E-03  3.828E-01  1.085E-01  3.404E-01  3.227E-02  9.033E+01  1.184E+02  2.377E+01
3.000E+01 -4.346E-03 -2.313E-03  2.808E-04  2.032E-03  2.825E-01  4.218E-02  3.727E-01  6.634E-02  1.046E+02  1.184E+02  2.377E+01
4.500E+01 -2.559E-03 -9.077E-04 -7.439E-04  1.652E-03  2.330E-01  2.010E-02  3.673E-01  9.380E-02  1.098E+02  1.184E+02  2.377E+01
6.000E+01 -1.792E-03 -4.184E-04 -9.554E-04  1.374E-03  2.010E-01  1.074E-02  3.541E-01  1.164E-01  1.140E+02  1.184E+02  2.377E+01
7.500E+01 -1.377E-03 -2.137E-04 -9.501E-04  1.164E-03  1.775E-01  6.217E-03  3.396E-01  1.353E-01  1.175E+02  1.184E+02  2.377E+01
9.000E+01 -1.134E-03 -1.191E-04 -8.961E-04  1.015E-03  1.589E-01  3.811E-03  3.258E-01  1.516E-01  1.205E+02  1.184E+02  2.402E+01
1.050E+02 -9.665E-04 -6.991E-05 -8.267E-04  8.956E-04  1.432E-01  2.433E-03  3.129E-01  1.659E-01  1.232E+02  1.184E+02  2.433E+01
1.200E+02 -8.381E-04 -4.264E-05 -7.578E-04  7.954E-04  1.297E-01  1.610E-03  3.010E-01  1.786E-01  1.256E+02  1.184E+02  2.460E+01
1.800E+02 -5.192E-04 -8.003E-06 -5.032E-04  5.112E-04  9.012E-02  4.123E-04  2.638E-01  2.168E-01  1.327E+02  1.184E+02  2.543E+01
2.400E+02 -3.460E-04 -2.174E-06 -3.417E-04  3.438E-04  6.463E-02  1.509E-04  2.389E-01  2.422E-01  1.374E+02  1.184E+02  2.597E+01
3.000E+02 -2.400E-04 -7.597E-07 -2.384E-04  2.392E-04  4.729E-02  7.126E-05  2.217E-01  2.594E-01  1.406E+02  1.184E+02  2.635E+01
3.600E+02 -1.710E-04 -3.305E-07 -1.704E-04  1.707E-04  3.511E-02  4.054E-05  2.096E-01  2.716E-01  1.428E+02  1.184E+02  2.661E+01
4.200E+02 -1.244E-04 -1.637E-07 -1.240E-04  1.242E-04  2.633E-02  2.645E-05  2.008E-01  2.803E-01  1.445E+02  1.184E+02  2.680E+01
4.800E+02 -9.180E-05 -9.018E-08 -9.162E-05  9.171E-05  1.991E-02  1.911E-05  1.944E-01  2.868E-01  1.457E+02  1.184E+02  2.694E+01
5.400E+02 -6.853E-05 -5.384E-08 -6.842E-05  6.847E-05  1.514E-02  1.491E-05  1.896E-01  2.915E-01  1.465E+02  1.184E+02  2.704E+01
6.000E+02 -5.160E-05 -3.416E-08 -5.153E-05  5.156E-05  1.156E-02  1.232E-05  1.851E-01  2.951E-01  1.472E+02  1.184E+02  2.712E+01
6.600E+02 -3.911E-05 -2.270E-08 -3.906E-05  3.908E-05  8.858E-03  1.065E-05  1.834E-01  2.978E-01  1.477E+02  1.184E+02  2.718E+01
7.200E+02 -2.979E-05 -1.563E-08 -2.976E-05  2.977E-05  6.805E-03  9.514E-06  1.813E-01  2.999E-01  1.481E+02  1.184E+02  2.722E+01
7.800E+02 -2.278E-05 -1.105E-08 -2.276E-05  2.277E-05  5.238E-03  8.724E-06  1.798E-01  3.014E-01  1.484E+02  1.184E+02  2.725E+01
8.400E+02 -1.747E-05 -7.981E-09 -1.746E-05  1.746E-05  4.038E-03  8.159E-06  1.786E-01  3.026E-01  1.486E+02  1.184E+02  2.728E+01
9.000E+02 -1.343E-05 -5.856E-09 -1.342E-05  1.343E-05  3.116E-03  7.748E-06  1.775E-01  3.035E-01  1.488E+02  1.184E+02  2.730E+01
9.600E+02 -1.034E-05 -4.351E-09 -1.034E-05  1.034E-05  2.407E-03  7.444E-06  1.769E-01  3.043E-01  1.489E+02  1.184E+02  2.731E+01
1.020E+03 -7.978E-06 -3.263E-09 -7.972E-06  7.975E-06  1.861E-03  7.217E-06  1.764E-01  3.048E-01  1.490E+02  1.184E+02  2.733E+01
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NOMENCLATURE

NOMENCLATURE

(B) - Concentration of catalyst

(Complex) - Concentration of complex

M_n - Number average mulecular weight

M_o - Molecular weight of the structural unit

(NCO) - Concentration of isocyanate

(NH_2) - Concentration of amine

(OH) - Concentration of hydroxyl compound

p - Extent of reaction

r - Ratio of initial concentration of diol to diisocyanate

R - Alkyl or aryl radical

(Sub. Urea) - Concentration of substituted Urea

X_n - Number average degree of polymerization

Nomenclature for the Computer Program

AMINE - Weight of diamine

CA - Concentration of diamine in foam mixture

CAO - Initial concentration of diamine in foam mixture

CB - Concentration of biuret

CNCO - Concentration of diisocyanate

COH - Concentration of diol

CONCO - Initial concentration of diisocyanate

COOH - Initial concentration of diol

CSUBU - Concentration of substituted urea

DA - Density of diamine

DADT - d(diamine)/dt

DBDT - d(biuret)/dt

DENSITY - Required foam density

DNCO - Density of diisocyanate

DNCODT - d(NCO)/dt

DOH - Density of diol

DOHDT - d(OH)/dt

DS - Density of surfactant

DSUBUDT - d(sub urea)/dt

DT - Time increment

EWNCO - Equivalent weight of diisocyanate

EWOH - Equivalent weight of diol

EXTREAC - Extent of reaction

FMXCNCO - Concentration of diisocyanate in foam mixture

HB - Heat evolved per mole of biuret formed

HEVOLVD - Heat evolved during crosslinking reactions

HF - Heat of vaporisation of Freon at its boiling point

HREQFTE - Heat required for the Freon to evaporate

HSUBU - Heat evolved per mole of substituted urea formed

Ko - Rate constant for diol-diisocyanate reaction

K1 - Rate constant for diisocyanate-diamine reaction

K2 - Rate constant for diisocyanate-disubstituted urea reaction

MO - Mulecular weight of a structural unit

MWNCO - Molecular weight of diisocyanate

MWOH - Molecular weight of diol

MWPREPM - Number average molecular weight of prepolymer

PRSENTF - Percent Freon required

RATIO - Ratio of hydroxyl to isocyanate groups required

RICONC - Ratio of initial concentrations of diol to isocyanate

SPHEAT - Specific heat of foaming mixture

SURFACT - Weight of surfactant

TEMP - Temperature

TWEIGHT - Total weight of the prepolymer mixture

TWNCO - Theoretical weight of diisocyanate required for a given weight of diol

VA - Volume of diamine

VFOAMMX - Volume of foam mixture

VNCO - Volume of diisocyanate

VOH - Volume of diol

VOL - Total volume of prepolymer mixture

VS - Volume of surfactant

WF - Weight of Freon

WFOAMMX - Weight of foam mixture

WNCO - Total weight of diisocyanate required

WOH - Weight of diol

XN - Number average degree of polymerization

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