A THESIS

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SEPARATION AND DETERMINATION OF VARIOUS ORGANIC AND INORGANIC SPECIES FROM AQUEOUS SOLUTION AND BIOLOGICAL SAMPLES USING NEW ANALYTICAL METHODS

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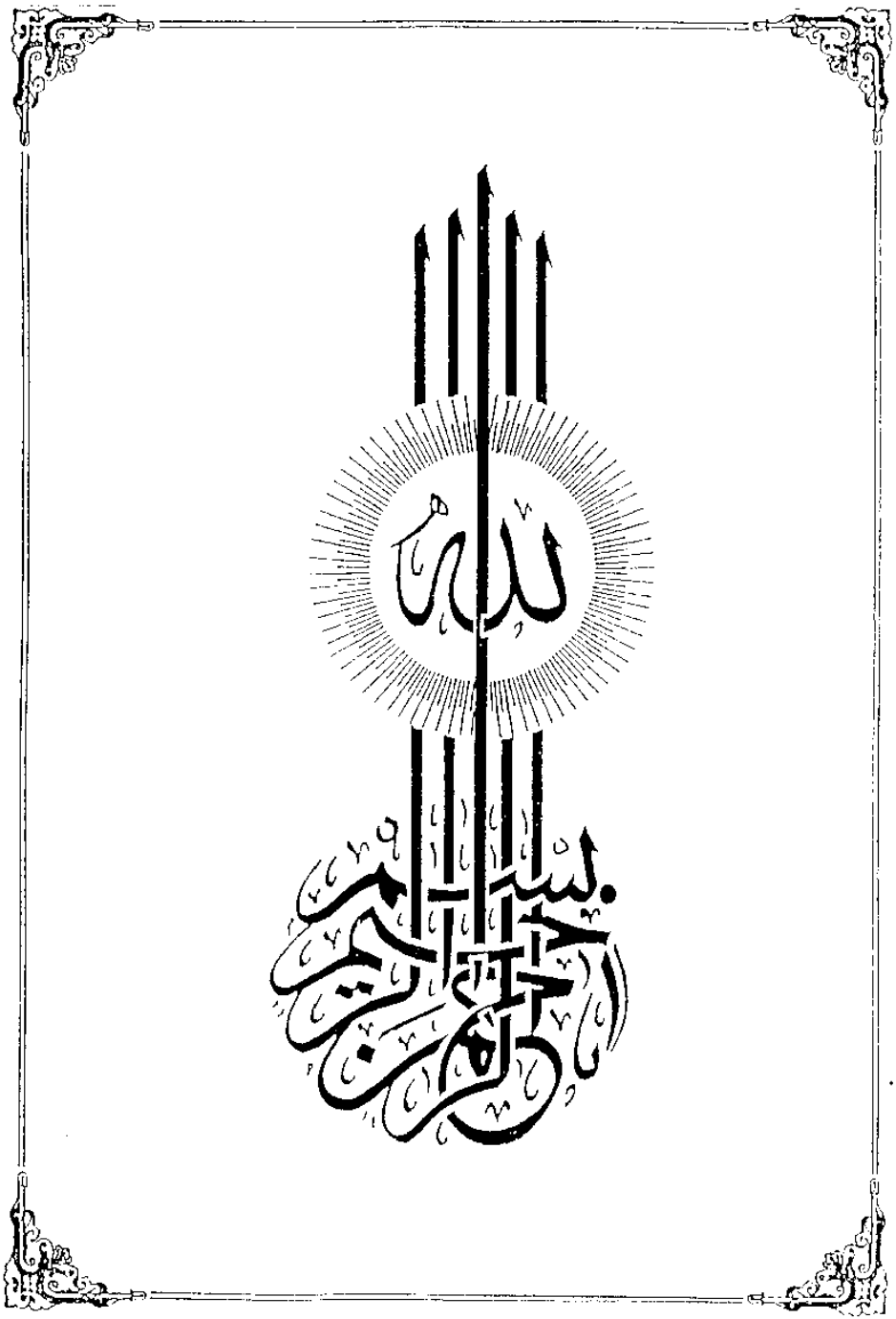

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SEPARATION AND DETERMINATION OF VARIOUS ORGANIC AND INORGANIC SPECIES FROM AQUEOUS SOLUTION AND BIOLOGICAL SAMPLES USING NEW ANALYTICAL METHODS

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CHAPTER I

CHAPTER (I)

Introduction

I. Introduction

Polyurethanes are manufactured annually in multi-million kilogram quantities for a wide range of markets. Such availability merits their exploitation for separation and concentration purposes in chemistry[1].

Several chemical and physical phenomena contribute largely to the property of polyurethane. Flexible and rigid foams of open and closed- cell structures with a wide range of properties have been prepared. Some fundamentals of cellular (foamed) plastics and their applications in analytical chemistry are considered in the present chapter.

1.1- Funamental knowledge of cellular plastics:

1.1.1- Foam definition:

Cellular (foamed) plastic can be defined[2] as plastic materials in which a proportion of solid phase is replaced by gas in the form of numerous small cells. The gas may be in a continuous phase to give an open cell material or it may be discontinuous, i.e. in the form of discrete, non-communicating cells. Low-density foams are dispersions of relatively large volumes of gas in relatively small volumes of solids having, for example, a

The polyhedral structure is clearly visible, and polyhedra must be pentagonal dodecahedra on the average. The polymer is distributed between the walls of the bubbles and the lines where bubbles intersect, with most of the polymer at the intersections[4]. The bubbles are called cells, the lines of intersections are called, strands, and the walls are called windows (or membranes). In an open cell flexible foam, at least two windows (from the total) in each cell must be ruptured for gases to pass freely through the foam. It is necessary for each window to be shared by two cells, and each strand to be shared by three cells.

1.1.3- Cell structure:

The cell structure (i.e. presence or absence of windows in the cells or the number of windows per cell) is a function of process by which the cellular material is made. It was noted that both rigid and flexible foams may be obtained with open and closed cells. The structure made up of windowless cells (containing only strands) is called reticulated foam[4].

It was reported[2] that, generally, flexible materials tend to have open cell structure while rigid materials tend to have closed cell ones. However, there are many

exceptions and as the type of cell structure is largely determined by the method of expansion,some materials which can be made by more than one method can exist in both open and closed cell forms. Furthermore, methods are available by which closed cell structure can be converted into the open cell form by rupture of windows. Rupturing may be caused mechanically by applying pressure or chemically by hydrolysis or oxidation.

1.1.4- General methods of preparation:

With the highly developed technology of making cellular plastics today[5], methods exist by which practically every plastic material may be made in the cellular form. The general principle for preparing cellular plastics is the dispersion of a gas phase in a liquid to obtain liquid foam which will then be solidified to a solid cellular plastic.

The main methods[2,6,7] for uniform dispersion of the gas bubbles are chemical, physical or mechanical.

Polyurethane foams are the most widely used cellular plastics in analytical chemistry. Consequently, their preparation will be considered here in some details.

CHAPTER (I)

INTRODUCTION

1.1.4.1- The fundamental chemistry of polyurethane foam synthesis:

Polyurethanes are substituted amide esters of carbamic acid, $R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-OH$, and are synthesized by the condensation - polymerization of polyesters, or polyols, with di-isocyanates and can be represented by the general equation.

$$OCNRNCO + HOR'OH \longrightarrow OCNRN\overset{HO}{\overset{|}{C}}OR'OH \qquad (1)$$

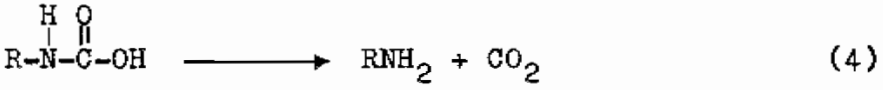
Here, R is commonly a low-molecular mass alkyl or aryl moiety and R' is typically an alkyl polyester or polyether chain. This basic urethane unite $-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-$ can then react further to give a long, linear polymer. This chain propagation is achieved by further similar condensations

$$OCNRN\overset{HO}{\overset{|}{C}}OR'OH + OCNRNCO \longrightarrow OCNRN\overset{HO}{\overset{|}{C}}OR'O\overset{OH}{\overset{|}{C}}NRNCO \qquad (2)$$

Or with a variety of agencies, for example, water or diamines, Thus, reaction with water forms an unstable carbamic acid,

$$RNCO + H_2O \longrightarrow R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-OH \qquad (3)$$

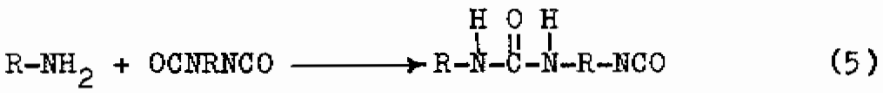
which decomposes to an amine and carbon dioxide:



$$R\text{-}\underset{\displaystyle H}{\overset{\displaystyle H}{N}}\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OH \longrightarrow RNH_2 + CO_2 \qquad (4)$$

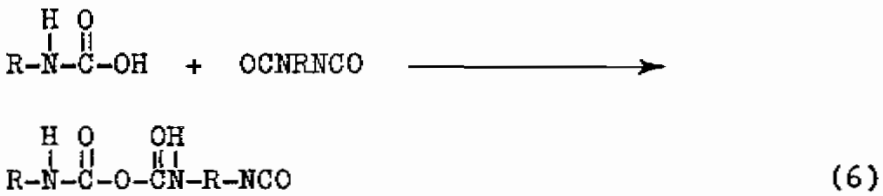
This isocyanate-water interaction is exploited for foam formation since the carbon dioxide liberated functions as a convenient in situ blowing agency. Silicons are also added as foam stabilizers.

The amine, from reaction (4) can also interact further with isocyanate entities and results in chain extension with the insertion of urea bridges:



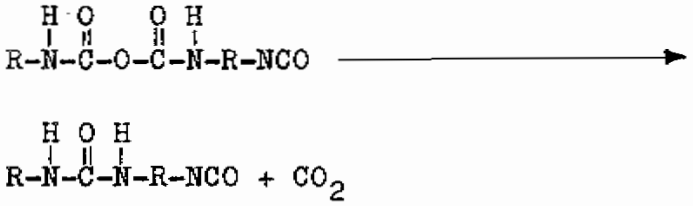
$$R\text{-}NH_2 + OCNRNCO \longrightarrow R\text{-}\underset{\displaystyle H}{\overset{\displaystyle H}{N}}\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}\underset{\displaystyle H}{\overset{\displaystyle H}{N}}\text{-}R\text{-}NCO \qquad (5)$$

On the other hand, the carbamic acid may react with isocyanate



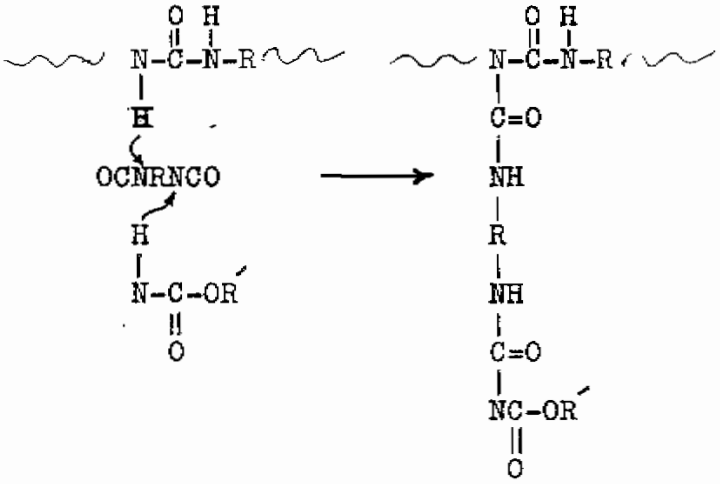
$$R\text{-}\underset{\displaystyle H}{\overset{\displaystyle H}{N}}\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OH + OCNRNCO \longrightarrow R\text{-}\underset{\displaystyle H}{\overset{\displaystyle H}{N}}\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}O\text{-}\overset{\displaystyle OH}{\overset{|}{C}}\text{=}N\text{-}R\text{-}NCO \qquad (6)$$

and the anhydride from equation (6) decomposes to give further blowing agency and urea bridges:



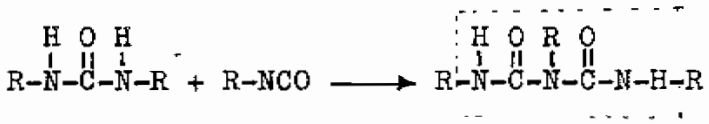
(7)

However, in addition to the primary chain propagation steps, side reactions lead to branching and cross-linking:



(8)

The synthesis is thus complex with possible reaction pathways resulting in the formation of products with biuret and allophonate units.



Biuret (9)

(10)

Allophanate

Depending on the nature of the diisocyonate-polyol condensation equation (1) the resulting polymer can take one of several forms, namely, flexible foams, rigid foams, synthetic rubbers coatings, adhesives, fibers, paints, and molding compounds. All these products come under the general heading of polyurethanes. Some are highly elastic with outstanding abrasion resistance as well as high resistance to tearing and extension - all features which are extremely important in their analytical applications.

Polyurethanes have been categorized in a variety of ways. On the basic of cell structure, urethanes are either open-cell or closed-cell foams. On the other hand, foams may be described as either high density or low density materials. Another classification is described in terms of flexible or rigid foams wherein the former types exhibit resilience and flexibility when subject to deformation, whereas the latter type is more resistant to deformation stress.

As previously mentioned, the basic ingredients in polyurethane foams preparation are the polyols and