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COMPOSITE MATERIALS FOR MAXILLOFACIAL PROSTHESES

Final Report

Harold L. Heller
Robert A. Erb, Ph.D.

February 1983

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The purpose of this program was to develop soft composite materials to be used as fillers in the fabrication of maxillofacial prostheses. Urethane shelled capsules containing polypropylene glycol were produced by interfacial polymerization process. Composites containing the capsules in elastomeric polymers lower the stiffness of the matrix polymer.

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## ABSTRACT

The purpose of this program was to develop soft composite materials to be used as fillers in the fabrication of maxillofacial prostheses. Elastomeric-shelled, liquid filled capsules having an average diameter of 2.3 mm have been developed as the composite system.

Urethane shelled capsules containing polypropylene glycol are produced by an interfacial polymerization process in which a polyurea skin is instantly formed over the droplet and a polyurethane inner surface is developed at a slower rate. An automatic system was designed and built for producing the capsules.

Composites of the capsules in elastomeric polymers have a lower stiffness than that of the polymers. The capsules can produce composites as soft as foams if the binding polymers are kept to a minimum amount required for holding the system together.

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CONTENTS

# 1. INTRODUCTION

The soft tissues in maxillofacial areas have complex mechanical properties, and are difficult to replicate when preparing external facial prostheses. An area in particular in which further improvement is needed in facial prothetics is in simulating the softness or "feel" of underlying soft tissues. This is particularly important if some movement capability is needed. The softest materials presently available are polymeric foams (which have the disadvantage of taking a permanent set by loss of gas when compressed) and gels (which are often unstable and sometimes lose internal liquid by syneresis).

External facial prosthetics, particularly where replication is of movable tissues, put hard demands on materials technology. Because the human soft tissues have complex mechanical properties which may vary from skin to underlying tissues and from place to place there is no single ideal material. Generally desirable properties for external maxillofacial prosthetic materials include:

1. Capability of being easily fabricated to various facial shapes and surface textures.

2. Ability to be colored internally and externally, with suitable translucency.

3. Mechanical properties (stress-strain behaviors) simulating those of skin and associated soft tissue.

4. Resistance to environmental factors, including sunlight, high and low temperatures, and humidity; retention of color and flexibility for extended periods of time.

5. Nontoxicity to host tissues and resistance to deterioration associated with contact with the host tissues.

6. Capability, if soiled, of being easily cleaned by soap and water, without loss of surface or marginal details.

7. Resistance to tear and abrasion when molded to very thin edges.

8. Ability to be bonded to living tissues with surgical appliance cements or other skin adhesives.

In this program a new class of materials was studied for use in fabricating maxillofacial prostheses: namely, liquid-filled, elastomeric-shelled microcapsules. Conceptually, such a product is attractive for several reasons: (1) the cells in the natural soft tissue are themselves composites of liquid (or semi-liquid) material in deformable shells; (2) the liquid-filled microcapsules could be stable entities free from the syneresis or gas-leakage of other soft materials; (3) the microcapsules could be stored as such and used by the prosthetist as an ultrasoft filler to modify other materials as needed.

Early in the program, efforts were directed toward producing microcapsules by two experimental approaches. One approach involved coaxial extrusion of a catalyzed elastomer precursor and core liquid into a receiving bath. The other approach involved the interfacial polymerization of polyurethane around droplets of a core liquid suspended in a continuum containing reactive materials. The most promising of the two systems was the interfacial polymerization process, and this approach was pursued throughout the program.

The interfacial polymerization system was developed to the point where liquid-filled capsules having an average diameter of 2.3 mm could be produced by an automatic system, and sufficient quantities of capsules were produced for testing in composites.

This report describes both experimental approaches and gives in detail the formulations and procedures necessary for producing urethane capsules.

-2-

## 2. HISTORY OF MATERIALS FOR MAXILLOFACIAL PROSTHETICS

Clark [1] at the beginning of his detailed book on prosthetics quotes
Sushruta Samhita (ca. 600 B.C.) as follows: "The love of life is next to our
love of our own face and thus the mutilated cry for help." Maxillofacial
disfigurements beyond the scope of restorative surgery arise from any sources,
including war wounds, accident trauma, birth defects, and radical surgery for
malignancies. Maxillofacial prothesis, the artificial replacement of parts of
the face and jaw, can help the disfigured person to be a functional part of
social, economic and other areas of life.

Prosthetics and materials have always been closely related. Among natural
materials used for facial prostheses, leather, wood, and metal could not
produce lifelike parts not only because they are too rigid, but also for the
basic reason that they are opaque whereas skin is translucent. Ordinary paint
coatings, being opaque themselves, will not solve the problem. Wax and glass
had translucency but were not durable and were too rigid to simulate facial
soft tissue. Vulcanite, a hard-rubber composition used by dental laboratories,
was used for facial-prostheses but also was opaque and too rigid.

In 1916, the first translucent and low-modulus material for prosthetics
was reported [2] as being used for artificial noses. This was a tinted
mixture of gelatin and glycerol. The hygroscopicity of glycerol would cause
fabricated parts to pick up moisture from the air or skin and lose their shape
after a few days. Addition of potassium dichromate reduced the tendency for
softening. Replacement of some of the glycerol by sorbitol [3] produced
prosthetics which could last a few months (Clarke's "synthetic flesh").

Rubber latex, unvulcanized and vulcanized, often used for a mold-making
material was also used in facial prostheses and was the best material for some
applications until the vinyl resins became available. Rubber latex has
problems with shrinkage, darkening with exposure to ultraviolet radiation, and
the relatively slow fabrication procedure.

The workhorse materials for maxillofacial soft-tissue prostheses for the
25 years after World War II were the highly-plasticized vinyl resins,
principally poly(vinyl chloride) and copolymers of vinyl acetate and vinyl
chloride. These are generally used in the form of dispersed systems
(colloidal sols) which gel irreversibly at elevated temperatures (typically
110-140°C). If the continuum is a nonvolatile plasticizer, the system is
known as plastisol; if volatile solvent is also present (usually to provide
the conversion at a lower temperature), the system is called an organosol. By
varying the ratio of plasticizer to resin the elastic modulus (stiffness) can
be predetermined over a wide range.

For prosthetics applications, proprietary compositions (e.g., Mediplas,
Flexiderm) have been available which have appropriate heat and UV stabilizers
added, and in some cases are tinted to simulate skin tones. Final custom
coloring is commonly accomplished by diffusion of oil-soluble dyes into the
composition.

For some prosthetics applications, solutions of plasticized vinyl polymers
(e.g., "Cordo Solution" [4,5] are used. In such cases evaporation of the
solvent is required during fabrication; thus multiple layers are needed to
build up thick sections.

The advantages of the plasticized vinyl compositions include:

1. Low modulus (though with considerable loss of tensile strength when
   approaching the moduli of soft tissue structures),

2. Castability with replication of minute surface details from molds,

3. Good dimensional stability compared with earlier low-modulus
   materials,

4. Translucency which can be varied, and

5. Colorability after molding by dye diffusion.

Disadvantages of the vinyl plastisols and organosols include:

1. The requirement for high temperatures in the molding process -- this
   prevents direct fabrication in agar and other moulage molds,

2. The high concentration of plasticizer in a gel structure leading
   sometimes to migration problems such as syneresis (formation of an
   oily surface film of plasticizer) or a solvent-type attack on
   surfaces such as lacquer finishes or polystyrene which the prosthesis
   might contact for a few hours,

-4-

3. Depletion of plasticizer from the outer layer of the prosthesis from volatilization or from washing with soap and water, leading to a stiffer surface than that present originally, and

4. Possible allergenic reactions from migration of plasticizers or from presence of necessary PVC stabilizers (absence of stabilizers can lead to HCl production).

Silicone elastomers of the polydimethylsiloxane type have been of interest because of their physiological inertness, their chemical stability, and their ability to be readily fabricated. Disadvantages of these materials include low tear and tensile stength (particularly for very soft compositions) and lack of materials combining transparency and good physical properties. One of the more promising silicone elastomers recently developed is Petrarch's PELD15 (Petrarch Systems Inc., Bristol, PA). This is a nearly transparent low durometer elastomer (A15) that may find some use in prosthetics.

Southern Research Institute [6] has been involved with the development of silphenylene polymers. These custom-synthesized silicone polymers provide very low modulus of elasticity, while maintaining good tear strength, ultimate tensile strength and elongation before break. At this time it appears that this type of polymer is not yet available for general use. Certain urethane elastomeric compositions can be used for maxillofacial prostheses. One publicized system [7,8] is a three-part polyurethane system, Epithane-3 (Daro Products). By varying the ratio of the ingredients it is reported that Shore A hardness from 5 to 50 can be obtained. The finished polymer has good transparency and reasonably long life (average reported to be nine months).

Our concept behind this project is that it should be possible to develop improved materials for maxillofacial prostheses within the context of multiphase systems, with our emphasis on the development and use of liquid-filled, elastomer-shelled capsules as ultrasoft fillers in prostheses. This type system would reduce the stiffness of any polymer in which the capsules are used.

## 3. DEVELOPMENT OF PRACTICAL TECHNIQUES FOR THE PREPARATION OF LIQUID-FILLED CAPSULES

### 3.1 REVIEW OF MICROENCAPSULATION TECHNIQUES

At the outset of this program, a basic question which had to be answered was which one or more of the many microencapsulation processes show the most promise for producing elastomeric-shelled microcapsules containing an inert liquid. While much of the diverse field of microencapsulation is proprietary, there are several reference books [9, 10, 11], in addition to papers and patents describing the various techniques.

General methods for microencapsulation include:

1) envelopment/coacervation (e.g., with gelatin walls);

2) emulsification/dehydration (or other solvent removal), including spray drying;

3) fluidized bed of core particles, spray coated;

4) fluidized bed of meltable coating material, with molten core droplets falling into it;

5) centrifugal forcing of core material through coating films;

6) electrostatic coating of aerosol droplets;

7) gaseous in situ polymerization (e.g., with p-xylylene) on the surface of solid (including frozen liquid) particles;

8) interfacial polymerization;

9) coaxial extrusion of core and shell material into a moving carrier-liquid stream.

Some of these methods are difficultly applicable to the encapsulation of liquids (particularly those with low freezing points) and some are not practical for use with suitable elastomeric materials for the shell. The last two approaches from this list, namely, coaxial extrusion and interfacial polymerization, are those which were chosen for making elastomeric-shelled, liquid-filled microcapsules. Both methods were pursued early in the program, but later full effort was given to the interfacial polymerization technique.

## 3.2 COAXIAL EXTRUSION METHOD

Coaxial extrusion is a process in which a core liquid is extruded through an inner tube and a shell-forming material is extruded through an annular space between the inner tube and a concentric outer tube. The material is extruded into a liquid bath. By stretching the extruded stream through movement of the liquid bath, and by interfacial tensions the extruded stream breaks into liquid-filled capsules.

A high-pressure coaxial extrusion system was designed and fabricated where it was found that the previous system, which used a variable-speed, torque-independent motor acting on a screw drive, could not provide adequate force on the piston actuators for fluid flow of elastomer precursor and catalyst. The new system, which is hydraulically actuated, is capable of delivering the elastomer-precursor liquid at pressures up to 4000 psi.

Figure 3-1 is a general view of the hydraulically actuated coaxial extrusion system. The hydraulic pusher is in the upper center and the control panel at the upper right. At the right is the variable-speed motor drive for the core liquid (in a 50 cc polypropylene syringe), with the speed control box at the far left resting on the variable-speed pump for the carrier stream. In the center of Figure 3-1 are the parallel cylinders containing the elastomer precursor and catalyst. The materials used were Silastic 382 Medical Grade Elastomer (a polydimethylsiloxane, Dow Corning), 4:1 with 360 Medical Fluid (20 centistoke polydimethylsiloxane fluid, Dow Corning), which gives a viscosity of about 100 poises. The catalyst used was stannous octoate (Catalyst M, Dow Corning), at about a 1% level.

The major problem to overcome with this system was the difficulty in stream-chopping the viscous elastomer-precursor material. Rotating and vibrating cutters became gummed up, and generally did not produce closed capsules from the coaxial stream. Open rotating cutters also produced too much turbulence in the receiving bath. Pulsed liquids were examined as a method for cutoff. Simpler systems -- such as opposed pulses from dental jets (e.g., Water Pik) -- did not work well. There were problems in alignment, good pulse shape, and need for varied pulse frequency.
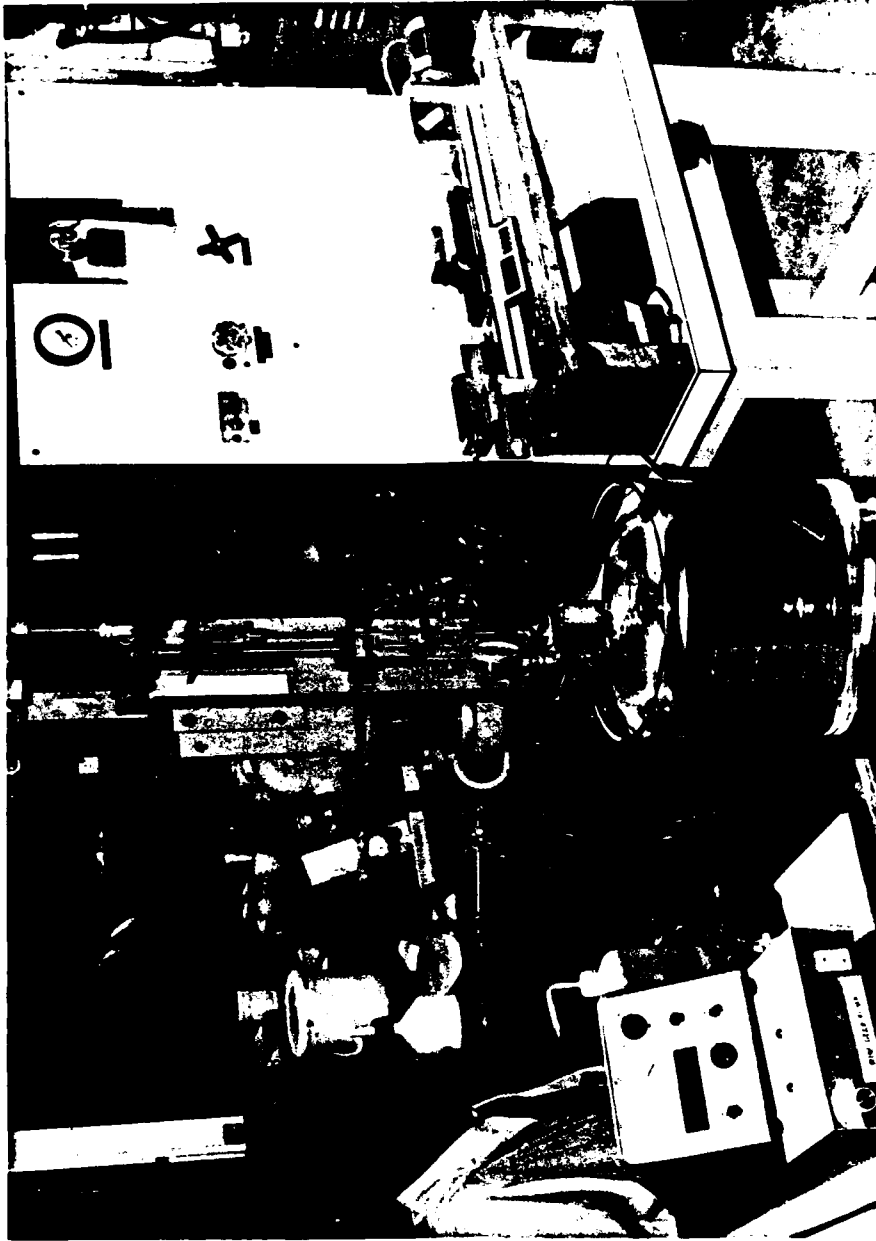
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FIGURE 3-1. General view of coaxial extrusion system for forming liquid-filled, elastomeric-shelled microcapsules.

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A more effective method was found to be an enclosed rotating blade built into an extrusion head. Figure 3-2 shows the extrusion head. The elastomer-precursor and catalyst enter, unmixed, from their respective piston pumps. These materials flow through the in-line static mixer, which is packed with curled stainless-steel ribbons. The mixed materials are then passed through a fine-mesh stainless-steel filter to remove any clumps of material that might clog the narrow extrusion annulus. From the filter the material passes into the annular region of the coaxial extrusion head.

The core liquid material (typically a polypropylene glycol) flows into the central channel. The coaxial stream is joined by a surrounding stream of carrier liquid which prevents the elastomer from sticking to the blade and walls and the triple stream passed through the enclosed rotating chopper. The carrier liquid prevents the elastomer from sticking to the blade and walls and provides a non-wetting barrier between each cut section. Figure 3-3 shows the extrusion head assembly from another angle to show the orifice for the chopped stream.

Initially water, and later, graded-density aqueous salt solutions were used in the receiving bath. The problem with aqueous systems had been that a slight imperfection or incompleted closure in the unsolidified wall of a capsule would not heal but would tend to open or remain open. This relates to the extremely hydrophobic nature of silicone polymers. With the aqueous receiving bath, most of the capsules formed were leakers. Use of a vegetable oil (soy oil) for the bath, with proper adjustment of the operating parameters, permitted capsules to close properly, with production of closed capsules approaching 100%. The oil is heated to accelerate the curing of the shell material.

The oil in the receiving tank was agitated by means of a magnetic stirrer. This helped to prevent the formed capsules from agglomerating while they were still tacky. Fabricated mesh bags were used to collect sequential samples of formed microcapsules during a run. The use of the collector bags permitted samples to be taken from each of several parameter settings during a run. Comparison among the samples helps to define the optimum parameters for the process. The overall parameters that can be varied, with some of these
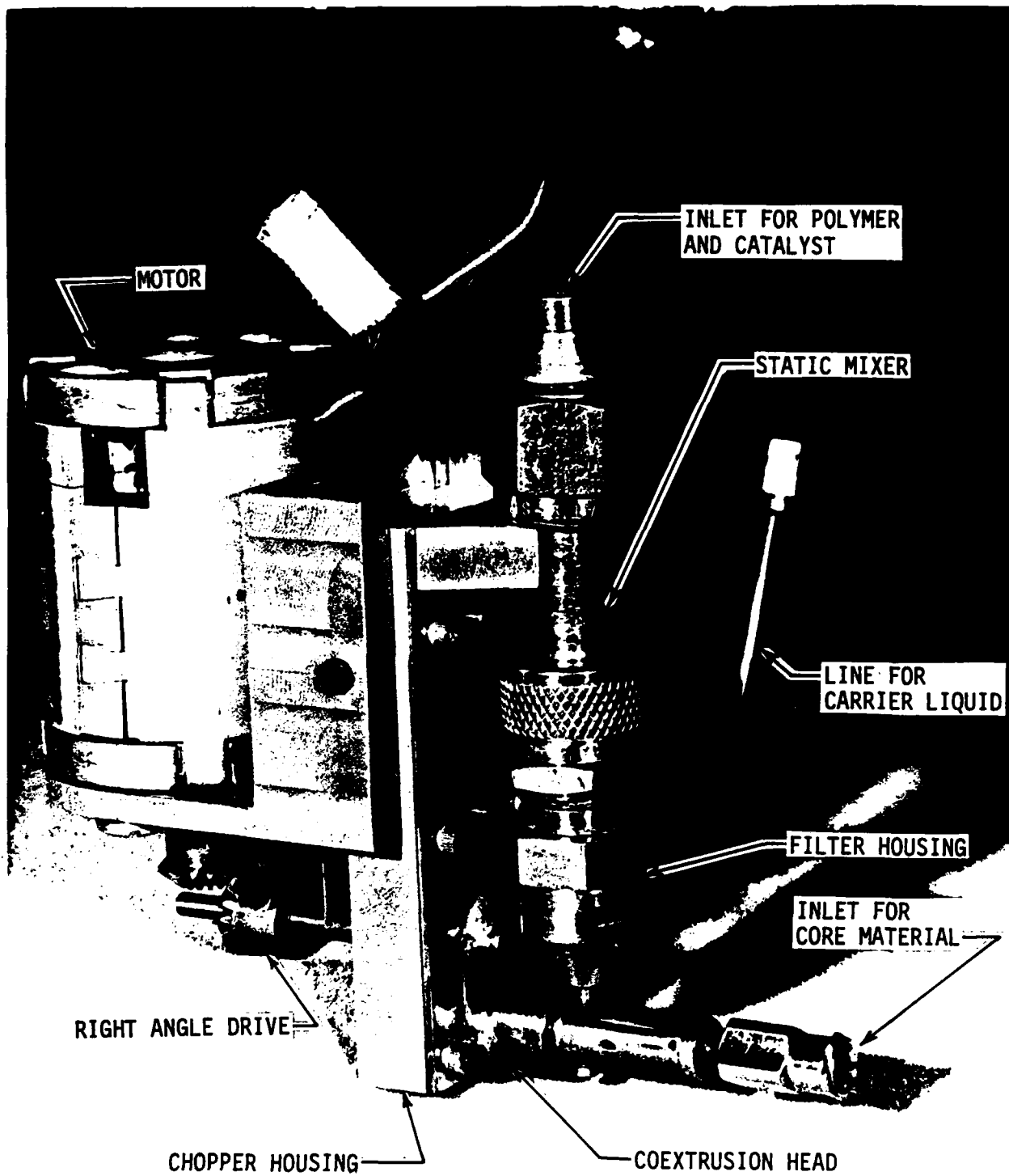
FIGURE 3-2. Extrusion head with enclosed chopper.

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FIGURE 3-3.   Extrusion head with enclosed chopper,
              showing orifice.

during a run, are: (1) pressure in the polymer/catalyst system (affecting the flow rate of shell material); (2) motor speed for the core-liquid flow actuator (affecting the flow rate of core liquid); (3) pump speed for the carrier liquid; (4) chopper speed; (5) bath temperature; (6) bath agitation rate.

Liquid-filled capsules were obtained with closed elastomeric shells, but a new problem became evident when shells free of pinholes were obtained. Transport by diffusion of core liquid into the shell caused dimpling after short-term storage. Systematic studies were carried out on weight pickup and swelling of Silastic 382 pieces in various core liquid. The most satisfactory material tests was polypropylene glycol 4000. This was successfully substituted for the polypropylene glycol 1200 used in developing the first sealed capsules.

## 3.3 INTERFACIAL POLYMERIZATION METHOD

Extensive experimental efforts were directed toward various reactive materials, the reaction parameters, and the resultant properties of formed shell material. A major problem had been to produce a wall which is elastomeric and reasonably strong by means of a polymerization reaction fast enough to be practical, and with a non-discoloring material system. To be avoided were pinholes in the formed walls, cure-through to form solid spheres and agglomeration of formed capsules.

In our initial attempts to define a wall composition with satisfactory mechanical properties, more than 60 experimental compositions were formulated, in a bulk screening test, using toluene diisocyanate (TDI) or hexamethylene diisocyanate (HMDI) reacted with diols, triols, tetrols, amines, and catalyst (stannous octoate). From these experiments a reaction system consisting of an intermediate MW diol (100 parts) and a low MW tetrol (13.3 parts), reacted either with TDI or HMDI, in the presence of a catalyst was chosen for further study.

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An interfacial liquid-drop method was used with diisocyanates in kerosene (constant or gradiant concentrations in a cylindrical tube) with drops of polyglycol mixtures with diamines and an inert material (UCON 50 HB-2000, to prevent formation of solid beads). With high diamine levels, a fast cure was obtained, but with excessively brittle walls; with lower amine contents elastomeric properties were retained with an unacceptably slow cure rate.

Studies of the above approach were abandoned for a more promising "prepolymer" method. In this approach, the monomers are partially polymerized by a method which produces low MW, liquid polymers with reactive terminals. These are later cured in a second step which completes the polymerization to (in this case) an elastomeric solid. Isocyanate-terminated (polyols plus excess diisocyanate) and acid chloride-terminated (polyols plus excess bis-acid chloride) prepolymers were studied as the core component with inert diluent liquid. With isocyanate-terminated prepolymer the external phase was a polyol plus organotin catalyst in kerosene, leading to a polyurethane wall; cure was too slow, however, and using diamines instead of polyol produced fragile shells. The acid chloride-terminated prepolymers were readily cured using diamines dissolved in kerosene to yield polyester beads. Curing rate was good, and properties of the formed wall material were very promising. The major problem encountered was a high fraction of leakers; approaches toward improving the percentage of closed shells included adjustment of the acid chloride/polyol ratio and the use of various other amine curatives. These approaches did not solve the leaking problem, but with refinements in the polyurethane system, more promising results were obtained.

In the improved system, kerosene (Fisher, deodorized, 96 wt. %), 1,7 diaminoheptane (Aldrich D1740-8, 1 wt %), and fumed silica (PPG Corp. Hi Sil T 600, 2 wt %) were mixed with a high speed mixer to form a thickened exterior phase. The silica thickener is required to control the rate of fall of the liquid droplets through this exterior phase during the rapid first stage of cure.

The interior phase consisted of:

(1) a mixture of linear and chain-branched isocyanate terminated prepolymers

(2) a mixture of linear and chain-branched polyols capable of reacting with (1) to form a polyurethane

(3) an amine catalyst (1,4 diaminobicyclooctane, "DABCO")

(4) an inert polar liquid

(5) a trace of non-reactive dye (eosin) to facilitate identification of the beads.

A linear isocyanate-terminated prepolymer (1 above) was prepared from a polyol (Pluracol 2010, BASF Wyandotte Corp, 200 g), methylenebidicyclohexyl isocyanate (Hylene W, DuPont, 62.4 g) and 1,'4-diaminobicyclooctane (DABCO, Air Products Co., 1.0 g) by mixing the reactants, under dry nitrogen and warming to 50°C for 4 hours. A chain-branched, isocyanate-terminated prepolymer was prepared from a mixture of:

| | |
|---|---|
| Pluracol P-2010 (Wyandotte) | 200.0 g |
| Pluracol PeP450 (Wyandotte) | 26.0 g |
| Hylene W (DuPont) | 190.0 g |
| DABCO (Air Products Company) | 2.3 g |

by mixing the reactants and warming them to 50°C for 4 hours.

The linear and branched chain prepolymers were mixed in the ratio 90 linear/10 branched (w/w) for use in capsule formation.

For the polyol mixture (2 above), P-2010 (97 parts) and PeP450 (3 parts) were mixed to form a reactive polyol phase capable of reaction with the isocyanate terminated prepolymers (1) to form a polyurethane. At ambient temperatures, the reaction time between (1) and (2) was 4-12 hours, even in the presence of catalyst (3), which allowed ample time for mixing and bead formation before the curing reaction occurred.

The inert polyol (4) (LB, 385, Union Carbide Corp.) and Eosin (5) were added as shown in the following basic interior phase formulation.

| | | |
|---|---|---|
| 1. | Linear Prepolymer | 39.60 g |
| | Branched Prepolymer | 4.40 g |
| 2. | Pluracol P-2010 | 11.52 g |
| | Pluracol PeP-450 | 0.36 g |

-14-

| 3. | DABCO | 0.12 g |
| 4. | Inert Polyol (LB-385) | 44.00 g |
| 5. | Eosin (for color) | trace |

The mixture was stable for 1-4 hours.

The freshly prepared internal phase (from above) was charged to a motor-driven syringe fitted with a suitable needle (a long, curved 22 gauge needle was found to be suitable for many preparations, but other sizes of needle can be used).

The internal phase was added dropwise to the curing bath (external phase) with the needle tip approximately 2-4 cm above the bath surface. A variable speed turntable was used to rotate the curing bath to provide a fresh surface for each droplet.

The droplets immediately formed a fragile (polyurea) skin. They were allowed to remain in the curing bath for one hour and were then removed from the bath (via the mesh basket), rinsed with a dilute nonionic detergent solution (1% Titron X-100, Rohm and Haas Company), dried and stored in a closed jar.

As initially prepared the capsules were fragile because of the low-strength, polyurea skin. However upon standing overnight the polyols present in the internal phase continued to react in the presence of catalyst to form a strong and tough, flexible, elastomeric capsule capable of extensive deformation without rupture.

It was found that these capsules were not compatible with castable elastomers due to severe cure inhibition. To overcome this problem, the DABCO catalyst was replaced with a tin catalyst. In doing so, a new internal phase formulation was developed using one isocyanate prepolymer.

The isocyanate used in this system was methylene-bis-(4-cyclohexyliso-cyanate) (Desmodur W; Mobay). It is used in the manufacture of non-discoloring urethane. It is sensitive to water and humid air and must be stored under a blanket of dry nitrogen. The stannous octoate catalyst was added to the isocyanate.

The polyols, Pluracol P-2010, a Wyandotte diol (98.7 parts) and Pluracol PeP-450, a Wyandotte triol (1.3 parts) are mixed to form a reactive polyol phase capable of reaction with the isocyanate to form a polyurethane. The polyol mixture is added dropwise to the catalyzed isocyanate under nitrogen.

The inert polyol core material initially used in this system was the LB-385 used in the earlier formulation, but it was found that it tended to prevent complete sealing at the tail end of the capsules. Replacing the LB fluids with polypropylene glycols overcame this problem.

The basic interior and external phase formulations used for capsule formation are shown in Section 5.2.

Retention time in the diamine bath had been reduced to about a half hour with this system, but it was found that with this long time in the bath, kerosene would permeate through the shells and form a microporosity that would allow a slow flow of the core material through the walls. It also caused a slow gelling of the core material. It was found that by reducing the retention time in the bath to about three minutes, the gelling could be prevented.

Other aging problems noticed with this formulation were stiffening of the shells and an indentation in the spherical shape over a period of time. While the indentation problem still exists to some degree, the increasing stiffness had been overcome by increasing the core material content to 75-80% of the formulation. The final formulation reflecting these changes is shown in section 4.2.

# 4. PROCEDURES AND CONSIDERATIONS IN PREPARING CAPSULES

## 4.1 SUMMARY

An effective and flexible process has been developed for the preparation of liquid filled polyurethane capsules of the type suitable for use in preparation of polymer composite systems.

This method utilizes a two-stage polymerization process in which a fragile polyurea skin is rapidly formed around a liquid droplet by interfacial polymerization as the first stage. After initial skin formation, a polyurethane wall membrane having the desired physical properties is formed by a slower, secondary process.

Capsules with strong, flexible wall membranes containing a variety of internal phases have been prepared by this method. The procedure developed from a manual single-drop method to an automatic system that can produce 90 capsules per minute. Higher production rates could be accomplished with a larger system.
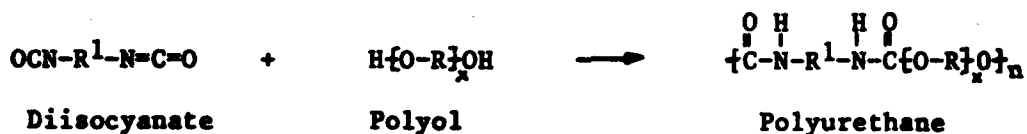
The urethane system used for the capsule wall is of the cycloaliphatic diisocyanate type used to produce low modulus, light stable, elastomeric films. The liquid interior phase preferred for maxillofacial prosthesis applications is a polypropylene glycol (Union Carbide Corp., PPG-2000).

The major problem throughout this program had been the identification of the many variables in the process, isolating them, and bringing them under control. The final results obtained from any variation usually required observing the capsules over a period of time, sometimes more than a month to notice any changes.

The preferred curing time for the droplets in the diamine bath is two minutes, but shorter times can be used in the automated production system if the freshly made capsules are stored in an inert liquid to prevent bonding together. A study of bath solvents has shown that only a narrow range of solvents can be used, and the preferred diamine is 1,7 diaminoheptane.
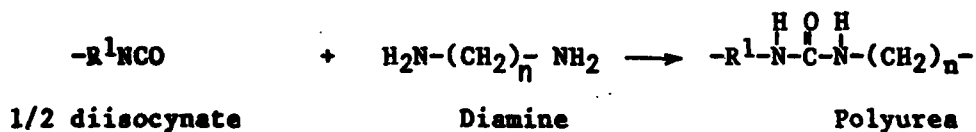
## 4.2 POLYMER CHEMISTRY

The diisocyanate used for the microcapsule shells is a cycloaliphatic produced by Mobay Chemical Corporation. Chemically, it is [methylene bis (4-cyclohexylisocyanate)], having the tradename Desmodur W. It is unstable, especially in the presence of moisture, and should be stored and used under nitrogen. The urethane is produced by an addition polymerization reaction using a mixture of linear and chain-branched polyols, the diisocyanate and stannous octoate as the catalyst. The chemical equation for this reaction is shown below.

$$OCN-R^1-N=C=O \quad + \quad H\{O-R\}_x OH \quad \longrightarrow \quad \underset{O\,H}{\overset{}{}}\,\underset{H\,O}{\overset{}{}}\,\{C-N-R^1-N-C\{O-R\}_x O\}_n$$

| Diisocyanate | Polyol | Polyurethane |
|---|---|---|

A diisocynate/polyol ratio is used which yields a five to six percent NCO excess. This free NCO content is all that is needed to provide a solution viscosity that can break up into droplets when using small amounts of the triol. Increasing the triol content increases the viscosity and produces a tougher urethane.

The second step in the formation of the microcapsules is the rapid formation of the polyurea shells. Diamines react very quickly with the remaining free NCOs, instantly forming a shell over the surface of the droplet. The chemical equation for this part of the process is shown below.

$$-R^1NCO \quad + \quad H_2N-(CH_2)_n NH_2 \quad \longrightarrow \quad -R^1-\underset{H\,O\,H}{\overset{}{}}N-C-N-(CH_2)_n-$$

| 1/2 diisocynate | Diamine | Polyurea |
|---|---|---|

The diamine is dissolved in a solvent in which the other components are not soluble. Before the addition of the urethane to the diamine solution, at least 50 percent more polyol is added. At this point, the remaining free NCOs react very slowly with the added polyol at room temperature.

Since the diamine reaction quickly forms a shell over the droplet, the internal liquid phase is insulated from further polymerization by this route. The remaining unused urethane in the core then slowly polymerizes on the inside surface of the capsule. The desired shell properties are achieved within several days, while further curing may continue for months.

## 4.3 EXTERNAL PHASE

### 4.3.1 Bath Solvents

The diamine bath had so many restrictions on it that when a system was found that worked, very little could be done to improve it. In order to function properly, the bath solvent must have the following properties:

1. The diamine must be soluble in it.
2. The diamine must be compatible with the solvent.
3. The liquid polymer droplets must not be soluble in it.
4. The core material must not be soluble in it.
5. The urethane shell must not be soluble or swell in it.

Besides these necessary requirements, additional desirable properties would include:

1. Low evaporation rate and low water absorption.
2. Low toxicity and fire hazard.
3. Easy wash-off from the capsules.

The only solvents that were found to be acceptable are aliphatic hydrocarbons having a boiling point above 150°C. Alcohols, ketones, halogenated and unsaturated aliphatics, aromatics and lower boiling aliphatics all have adverse effects on the diamines or the capsule materials.

Kerosene with a boiling range of 190-261°C is an acceptable solvent for the bath. The microcapsules start to swell when left in it over 10 minutes, and there also appears to be a limited solubility of the diamines in it. When the droplets of the urethane/core material are fed into the bath at a rate fast enough to produce an oversaturation of a given volume of solvent, the curing time needs to be increased, but returning to a lower number of droplets, the two minute cure in the same bath is satisfactory.

-19-

Varsol No. 1, an Exxon narrow-cut mineral spirit (distillation range 151-202°C) has been found to be a suitable solvent for the bath. The preferred solvent, however, is Exxon Isopar G. It is a narrow-cut isoparaffinic hydrocarbon with a boiling range of 156-176°C. The diamine is more soluble in it, the Cab-O-Sil thickener disperses more easily in it and there is less of a problem with the shells swelling in it.

It was thought that petroleum ether and hexane would satisfy the first five requirements mentioned above, but the low densities of these solvents require the addition of more Cab-O-Sil to prevent the microcapsules from hitting the bottom of the container. The evaporation rate with these solvents was so high, that the Cab-O-Sil tended to form hard crusts around the surface edges and on the nylon basket. These crusts contained degraded diaminoheptane and presented a problem in handling on an automated system. Removal of the crusts and replenishment of the reagents was a necessary and undesirable part of the process.

A closer look at the low boiling solvents such as hexane showed that the crusts formed at and above the surface of the solvent were vapor deposited diaminoheptane which had reacted with moisture in the air. We are not interested in low boil solvents for the bath due to this problem and the swelling of the capsule shells, but hexane is used as a quick rinse after the microcapsules are removed from the bath.

## 4.3.2 Bath Thickener

Cab-O-Sil, a fumed silica powder, is used to thicken the bath solvent so that the freshly formed microcapsules do not settle to the bottom too quickly. Three percent Cab-O-Sil had been used to achieve the optimum thickening, but now this quantity has been reduced to 1.3 percent by using a unique dispersing technique. This method consists of simply adding the Cab-O-Sil directly to the solvents and then inserting an energized ultrasonic horn into it for three seconds. Complete dispersion is accomplished in that time with Cab-O-Sil M-5.

The low amounts of Cab-O-Sil that are used are not enough to produce a stable suspension, so some agitation is needed to prevent the formation of a denser layer near the bottom of the bath.

### 4.3.3 Diamines

A series of diamines was evaluated to find if there was a more soluble one, and to see if the chain length had any effect on the elasticity of the shells. The three to twelve carbon chain diamines were examined. The chain lengths below six carbons were not evaluated because 1,3 diaminopropane is a severe poison, and the four and five carbon chain diamines have very foul smells and were set aside for this reason. The six carbon chain diamine (1,6 diaminohexane) appears to be the most soluble one of the series and works well but absorbs water faster than the others. At the present time, it has no distinct advantages over the 1,7 diaminoheptane that is used as our standard.

The poorest diamine of the series is the 1,12 diaminododecane. Its lower solubility may account for its inability to form a shell over the droplets. The 1,8 diaminooctane bath produced droplet shells that were too fragile to be handled, but the 1,9 diaminononane bath produced good quality microcapsules. Overall, the 1,7 diaminoheptane bath is still the best since no significant improvements in the elasticity of the shells were found with the other diamines that worked.

### 4.4 INTERNAL PHASE

### 4.4.1 Urethane Shell

The elasticity of the capsule shells depends upon the ratio of the straight chain to branched chain polyols used. Straight chain diols impart elasticity and the triols provide stiffness. Capsules can not be formed by just using diols alone, and triols can not be used alone because they produce a liquid that is too stiff to form droplets. The upper limit for the triol concentration is only a few percent due to the high viscosity it produces, but this is as much or more than is needed. An increase in the triol

-21-

concentration would require an increase in the free NCO content to maintain the same viscosity. It is necessary to work at the upper viscosity limit to achieve the desired shell properties. It is also necessary to use a long chain polyol for the core material, and with this combination, tails sometimes form on the microcapsules.

The formation of tails on the microcapsules is not a serious problem when they are formed as a solid strand. Tails have been formed in some batches that are hollow and poorly sealed at their ends and other batches have produced short large diameter tails. It has been found that the problem varies with the rate from which the liquid polymer of a given viscosity is forced out of the syringe needle. The optimum rate for producing droplets is a rate at which the droplet will fall free before an additional amount of material is formed at the end of the needle. The additional material is pulled along as an extension on the droplet. Increasing the droplet formation rate increases the droplet length, and eventually at a still higher rate, forms a continuous stream. Therefore, the optimum rate at which droplets can be made is controlled chiefly by the viscosity of the liquid polymer. The optimum rate of drop formation can be pushed slightly higher by increasing the length of fall for the droplet, but this too has its limits. There is an optimum height which allows enough time for the droplet to pull together and form a sphere before it hits the bath. Increasing the distance allows more time for the tail to be drawn in, but a point is reached where the tail begins to increase in diameter. This appears to be due to distortion from the higher impact on contacting the bath. To determine the correct height for a given formulation, single droplets are manually dropped at different heights and then examined for tails.

The method used for preparing the urethane has been simplified. In the earlier formulations, the isocyanate and the catalyst were placed in a waterbath heated vessel and the polyol blend was added dropwise into it. The entire system was under flowing nitrogen and constantly stirred until the polyols were completely added.

A simpler method used for small batches (100-200 gms) is to add all but the catalyst into a jar containing a magnetic stirrer, and blending these for a short time. The catalyst is added and nitrogen is flowed into the jar which is then closed and allowed to stir for several hours. The jar is not opened until ready for use.

When new formulations are prepared, they are first tested for elasticity by forming a polyurea strip. To do this, the prepolymer is brushed on a thin metal sheet and then placed in the diamine bath for two minutes. The film is rinsed, carefully dried and then cut free from the substrate. It is then placed on a polyethylene sheet and pressed to remove the core material. The film is wiped clean and left in place for 24 hours before it is tested. Our best formulations produce films that can be stretched from 400 to 600 percent before breaking.

### 4.4.2  Core Material

The preferred core material is Dow Polyglycol P2000. It was found that the high molecular weight polyols had less of a tendency to bleed through the capsule shells than the lower molecular weight ones.

The polyglycol P2000 is added to the urethane and allowed to stand for one day before microcapsules are made from it. After standing for one day at room temperature, it is stored in a freezer to prolong its usefulness.

The P2000 concentration had been increased from 50% to 75% over a period of time. As the concentration is increased, the length of time that the shells remain fragile is increased, so the benefits of this move were not immediately or easily noticed. The benefits of this move are to reduce the viscosity of the mix and to provide softer shells.

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# 5. CAPSULE PRODUCTION

## 5.1 EQUIPMENT

An automated system was designed, built and used for producing capsules. The system consists of a stainless steel trough with a sloping bottom that is 2.5 inches deep at one end and tapers to the surface over an 18 inch length. A belt is fed through the trough, carrying the microcapsules out of the solvent at the shallow end. The nylon mesh belt travels under the trough, under a tension pulley, over the variable speed drive gear, then around the deep side of the trough. The droplets are added at about the midpoint in the trough and slowly settle to the belt, by which time sturdy shells are formed. A unique feature of the bath is that a counter current is formed by the movement of the belt so that the droplets flow to the rear providing a clear area for each following drop. With proper adjustment, the capsules settle on the belt at the back end and are carried forward over the entire length. A simple sketch of the system is shown in Figure 5-1. A Record of Invention form is on file at FRC for this apparatus.

The belt is made from nylon screening having 1.35 mm square openings. It is sewn together at the ends with fine nylon threads to provide a continuous belt. The system is designed so that it can be easily disassembled for cleaning.

Initially the belt rode flat against the bottom on the inside of the trough, through the liquid and out above the liquid level, but it was found that the solvent was carried out over the top in the openings of the belt. Four millimeter diameter glass rods were mounted under the belt at the midpoint and top end of the trough to allow the solvent to flow back, but it still remained in the pores of the belt and drained out on the tension pulley. The solvent in the pores also held the capsules tenaciously to the screen.

To overcome this problem, an air jet was added to blow the solvent out of the belt at the upper end of the trough, but this did not help release the microcapsules. Another air jet had to be added under the belt on the underside of the trough to blow the microcapsules free. One final problem was the build-up of Cab-O-Sil at the upper end of the belt. After a short time of
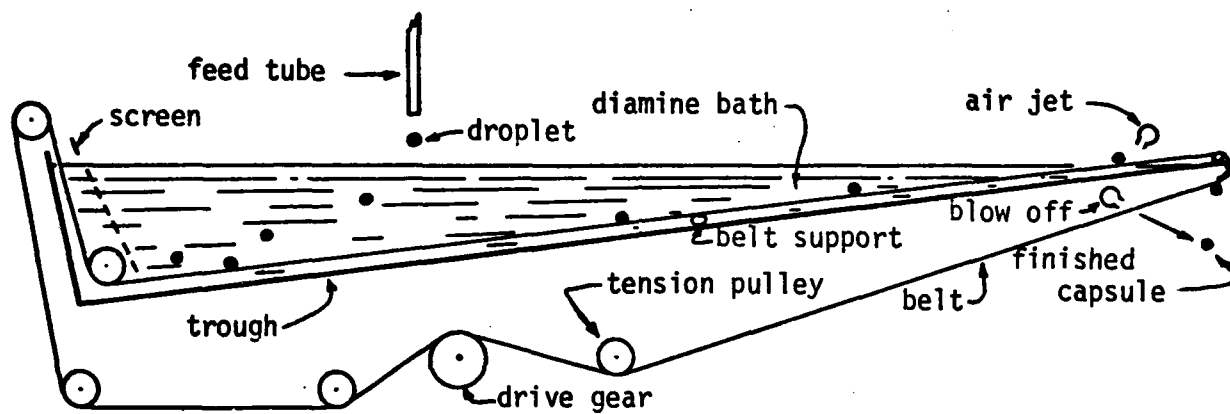
FIGURE 5-1.   Diagram of Automatic Microcapsule Production System.

running a thick paste would develop around the belt where it lifts out of the liquid. This was overcome by adding another glass rod under the belt about one-third of the way down the trough. This acts as a wiper and keeps the belt from touching the bottom of the trough.

The feed mechanism consists of a Unislide drive that operates two five cubic centimeter syringes. One of the syringe needles is about 3 milliliters shorter than the other so two separate columns of drops are formed. This arrangement is shown in Figure 5-2. A feed rate is selected that produces droplets with minimum tail formation. Figures 5-3 and 5-4 show the complete setup. The syringe size could be larger and at least one more syringe could be added to the present system. With the present system, a production rate of 80 capsules per minute is possible.

When the system is in operation, the bath is enclosed with Saran wrap to keep moisture out. The film is draped over the trough, leaving only the ends exposed.

The proper location for the droplets to enter the bath is detected by watching the settling rate of the first droplets that enter the bath. The distance that they are carried by the countercurrent depends on the degree of thickening and the belt traveling rate. If the droplets do not sink to the belt in time, they are drawn through the belt pulley and crushed. A stiff screen could be placed over the pulley as shown in Figure 5-1.

## 5.2  PREPARATION OF CAPSULES

The diisocyanate is charged into a glass jar containing a magnetic stirring bar. The prescribed quantity of the polyol mixture is then added to the jar and stirred for 15 minutes. The catalyst is then added using a microliter syringe. Air is purged from the jar with nitrogen and the lid is applied. This mixture is then stirred for at least two hours at room temperature, allowed to stand overnight, and then stored in a freezer until ready for use. At this stage there is a 5.4% excess of free NCO.
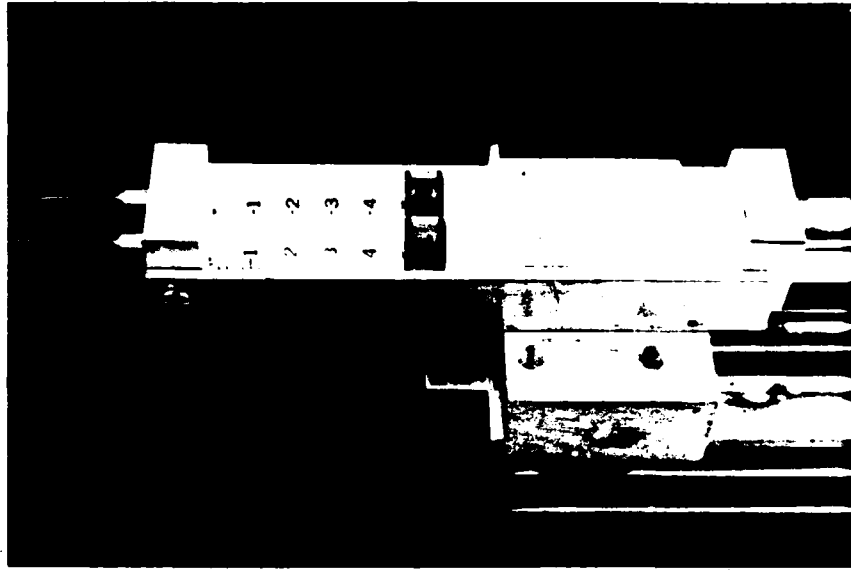
FIGURE 5-2. Dual Syringe Arrangement for Producing Liquid Droplets.
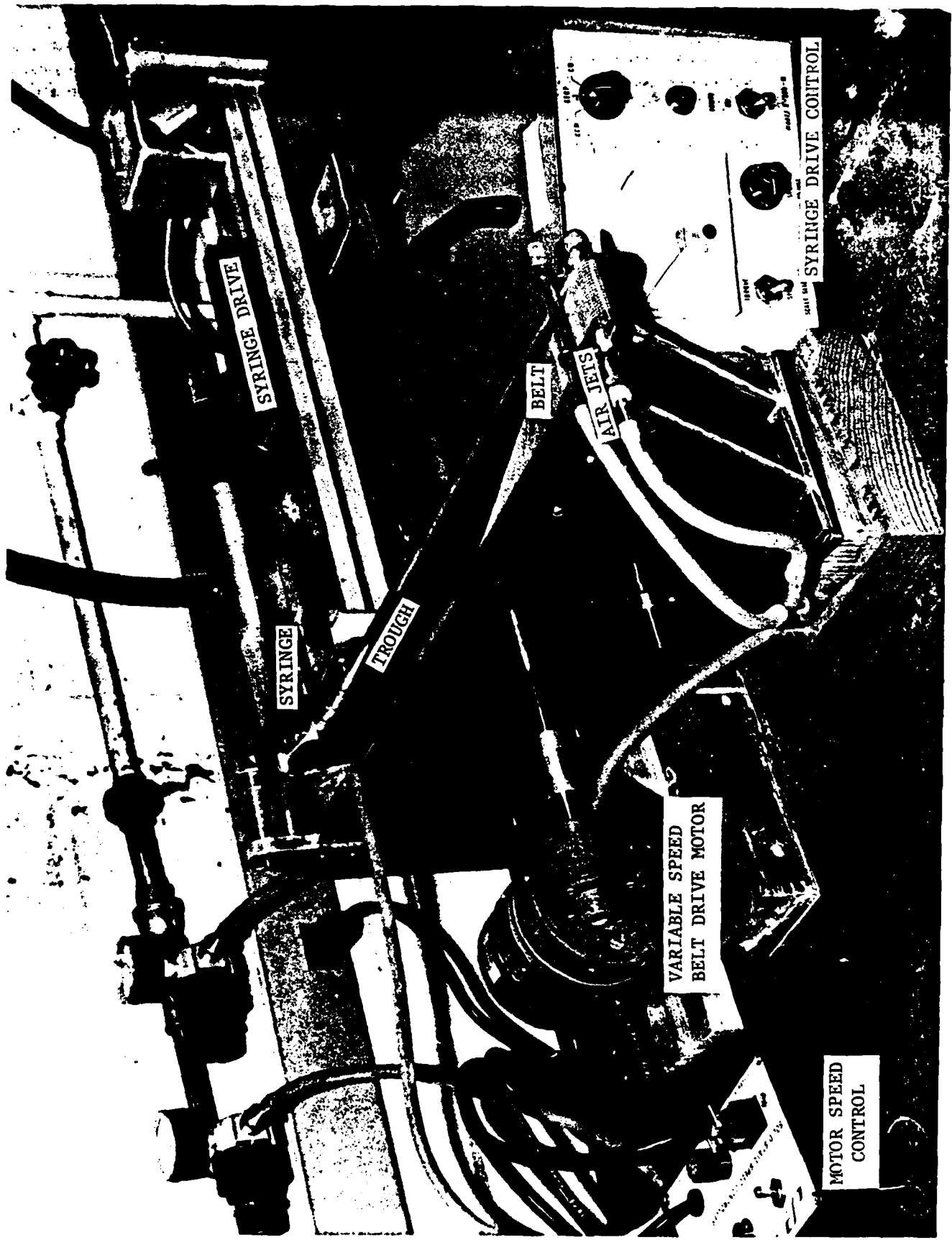
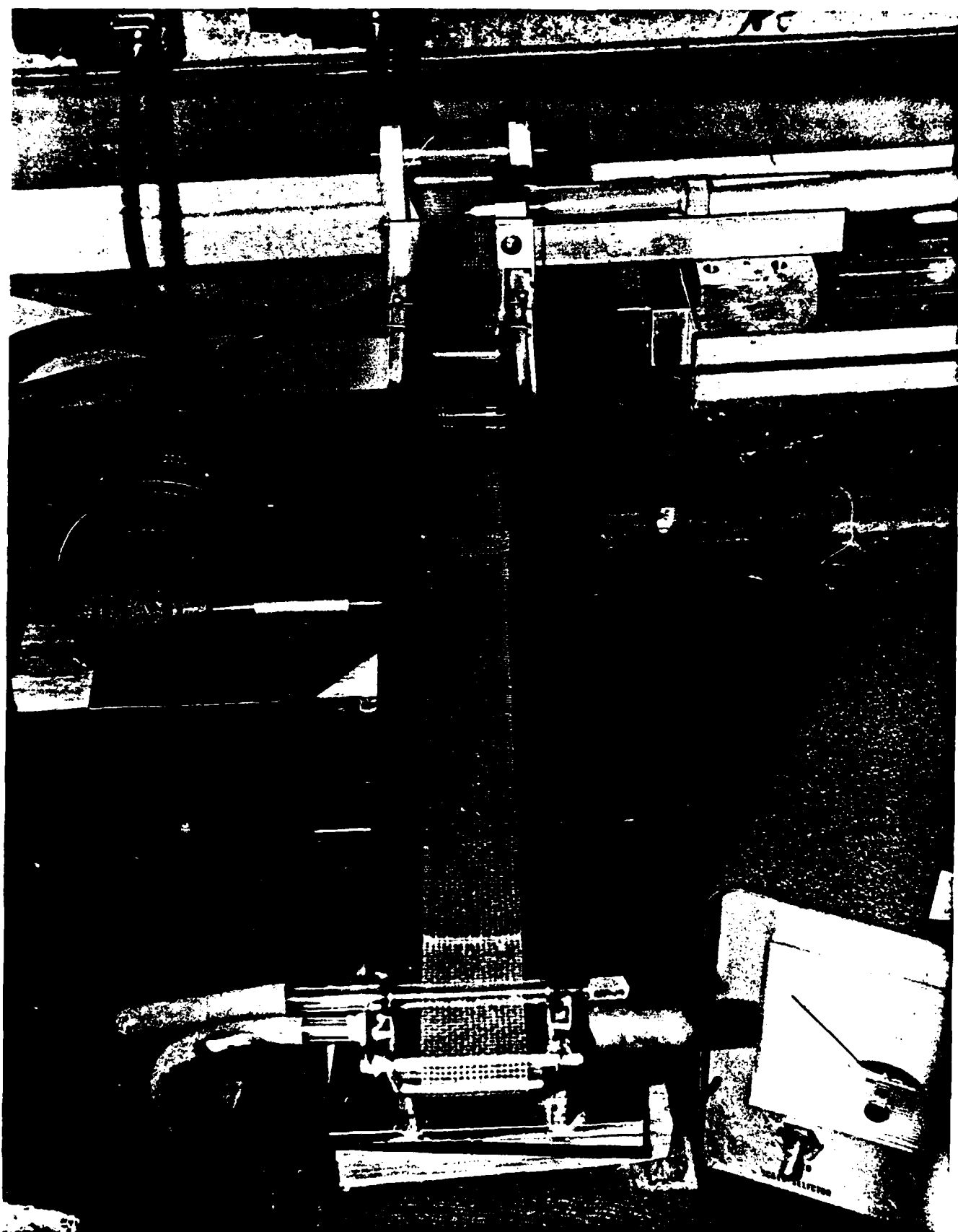FIGURE 5-3. Automatic Microcapsule Production System.

FIGURE 5-4. Automatic Microcapsule Production System (Trough Empty).

Before use, the urethane prepolymer is brought to room temperature. The desired quantity is added to a bottle containing the core material (PPG-2000) and the dye, and thoroughly stirred. Nitrogen is then flowed into both glass containers, and the prepolymer is placed back in the freezer. The bottled liquid is held at room temperature for at least one day before using. The remaining free NCOs react very slowly with the added polyol providing sufficient time (days) for its use.

It is best to use a freshly prepared bath. The Cab-O-Sil should be dried in an oven at 110°C for several hours before use to remove any free moisture. Upon drying, it is added to the solvent and dispersed with an ultrasonic horn. The diamine is melted, added to this mixture and stirred in well. If it is not used immediately, it should be stored in a closed container.

The following formulations are recommended:

### Interior phase

| Materials | | Percent (wt.) | |
|---|---|---|---|
| Desmodur W | | 27.3 | |
| Pluracol PL-2010 (Wyandotte) | 98.7 | 72.6 | 75 |
| Pluracol PeP-450 | 1.3 | | |
| Stannous octoate (Dow Corning) | | 0.1 | |
| PPG-2000 (Union Carbide) | 100.0 | – | 25 |
| Eosin | trace | | |

### External Phase

| Materials | Percent (wt) |
|---|---|
| Isopar G (Exxon) | 97.7 |
| Cab-O-Sil M-5 (Cabot) | 1.3 |
| 1,7 diaminoheptane (Aldrich) | 1.0 |

For production, the bath is filled and four syringes are charged (two extras for the next run) and two are mounted in the drive. The belt is set in motion and the syringe drive is started at a slow rate. The initial drops are observed for complete settling before they reach the back of the bath, and if satisfactory, the drop rate is set to the desired rate. The air jets are turned on before any capsules come out of the bath. The air flow is adjusted to a level high enough to blow off the capsules.

A large receiving bath is needed for collecting the capsules. This is preferably a wide container having 2 to 3 cm of kerosene in it. The kerosene is needed to hold the tender capsules in a spherical shape and to prevent sticking together.

The capsules collected in the kerosene are removed when the syringes are replaced. They are then rinsed for 5-10 seconds in hexane which is decanted off, and spread out to dry on paper. At this stage, the capsules are quite tender and require several days of aging before they can be used. The average capsule size is 2.3 mm in diameter. Figure 5-5 shows a handful of month-old capsules, and Figure 5-6 shows capsules with tails.
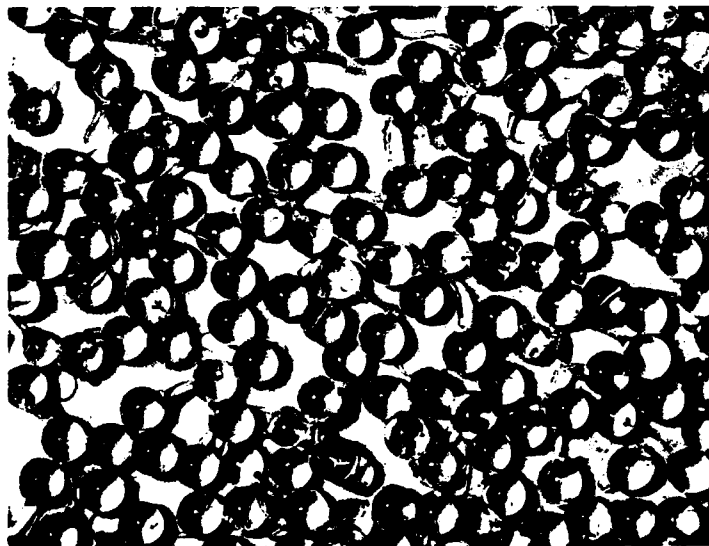
FIGURE 5-5. Handful of Month-Old Capsules.



FIGURE 5-6. Liquid Filled Capsules With Tails (2X).

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# 6. MECHANICAL TESTING OF CAPSULES

Bulk testing of the capsules was not possible before the successful switch to the stannous octoate catalyst due to the cure inhibition of the matrix elastomers by the previous catalysts.

Initially, single microcapsules were tested under a compressive load using strain gauges and a depth micrometer. This method of measurement was employed not so much for determining the properties of the capsules, but for the stiffening of the shells on aging for each formulation. A stress-strain curve for a typical freshly made capsule is shown in Figure 6-1.

From the initial straight line portion of the curves obtained for capsules under compression as seen in Figure 6-1, and using an equation derived for determining the compressional stress for any strain, the modulus of a single capsule could be found. This equation is given below:

$$S = \pi \left[ \left( \frac{1.33R}{d} - 0.013d^2 \right)^{\frac{1}{2}} - 0.393d \right]^2 \bigg/ L$$

where S is the compressive stress of the capsule, and:

L = the applied load

R = the original radius of the sphere before compression

d = the distance between the compression plates at any given L.

The modulus is the stress-strain ratio at any point on the initial straight line section of the curve. The modulus for a typical capsule is 600 $gms/cm^2$. This value correlates well with the modulus found for the bulk value of capsules.

Matrix elastomers of Dow Corning MDX 4-4210 Clean Grade Elastomer, Silastic 382 Medical Grade Elastomer Medical Adhesive A, and RTV 3145 can now be used without inhibition from the urethane catalyst. Figure 6-2 shows a cut cross section of capsules imbedded in MDX 4-4210. Dow Corning Q7-2218 silicone gel and Petrarch Systems PEHP-150 silicone elastomer can not be used due to mild cure inhibition.
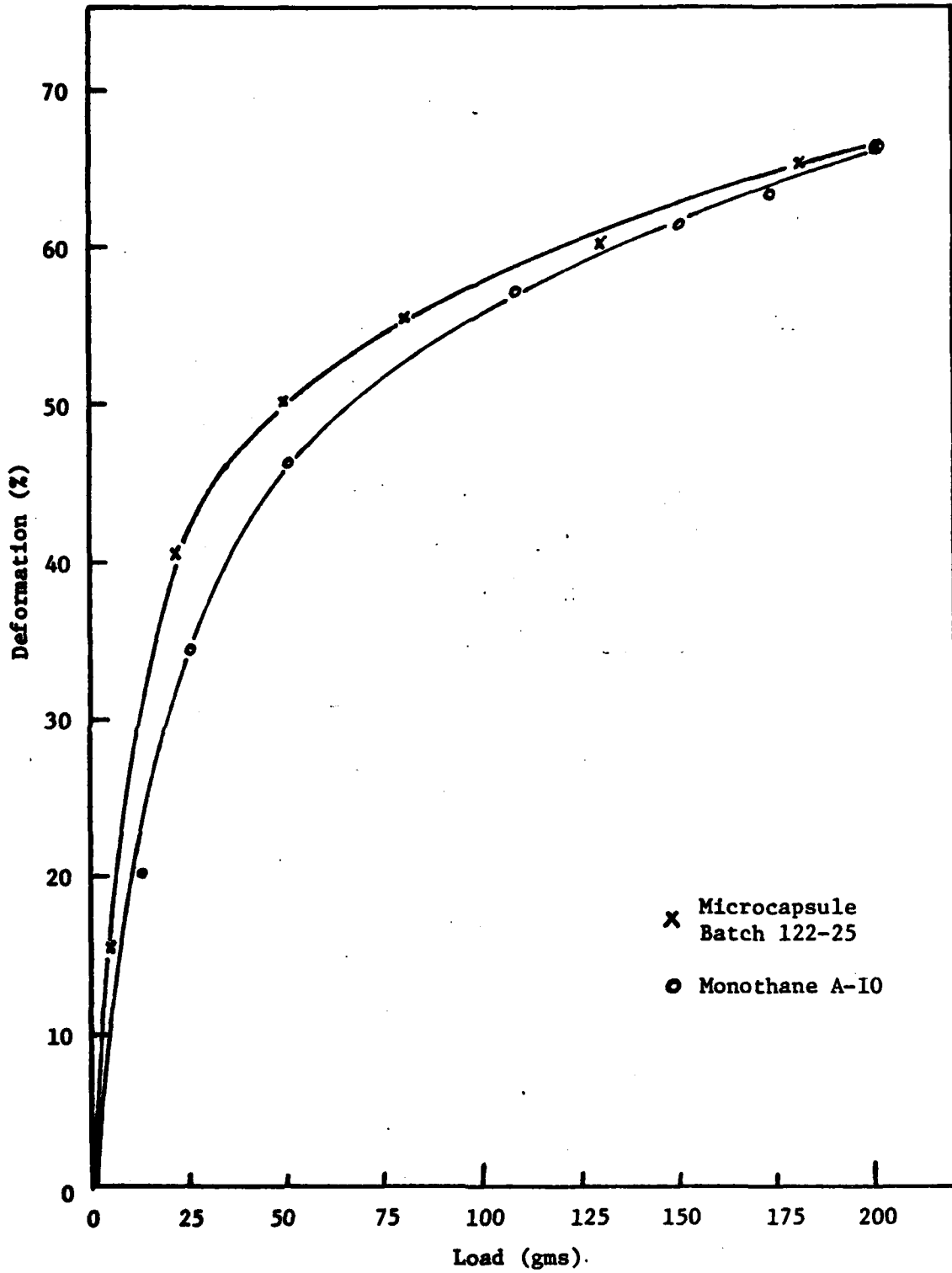
-33-

FIGURE 6-1.   Compression Loading of
              Single Elastomeric Beads

-34-

FIGURE 6-2. Cut Cross Section of Capsules in MDX4-4210 (12X).

Solvent based elastomers evaluated as matrix binding materials include Shell Kraton G1657 thermoplastic rubber (styrene-butadiene-styrene block copolymer) and Dow Corning 355 medical adhesive. These systems bond the capsules together without filling in the void spaces.

A full range of capsule loadings in MDX4-4210 were evaluated by compression testing cylinders (1 inch high by 0.75 inch diameter) of the composites. The compression rate used was 2.0 inches/min. The modulus of each cylinder was calculated for the initial straight-line portion of the curves. These results are shown in Figure 6-3. The value obtained for no binding material was obtained by lightly pressing the capsules in a beaker and applying the load with a flat plunger into the center of the mass. This value is lower than the value obtained for a single capsule due to the air voids in the mass. The value obtained for the sample containing 14% MDX4-4210 contained 9% air; all of the others were solid silicone/capsule composites.

In addition to the MDX4-4210 composites, cylinders of composites using other binders, and other soft materials without capsules in them were evaluated. These materials and their modulus values are given in Table 6-1.

Table 6-1: Initial Modulus Values for Some Soft Materials and Composites

| Materials | Composition | Modulus (gms/cm$^2$) |
|---|---|---|
| Urethane capsule | one liquid filled capsule | 600 |
| 355 Medical Adhesive | coated capsules | 670 |
| Kraton G-1657 | coated capsules | 710 |
| Q7-2218 gel | enough gel to fill voids between capsules | 120 |
| Q7-2218 gel | all gel | 220 |
| Eccofoam FPF[1] | all urethane foam | 630 |
| Q7-4290 prosthetic foam[2] | all silicone foam | 580 |

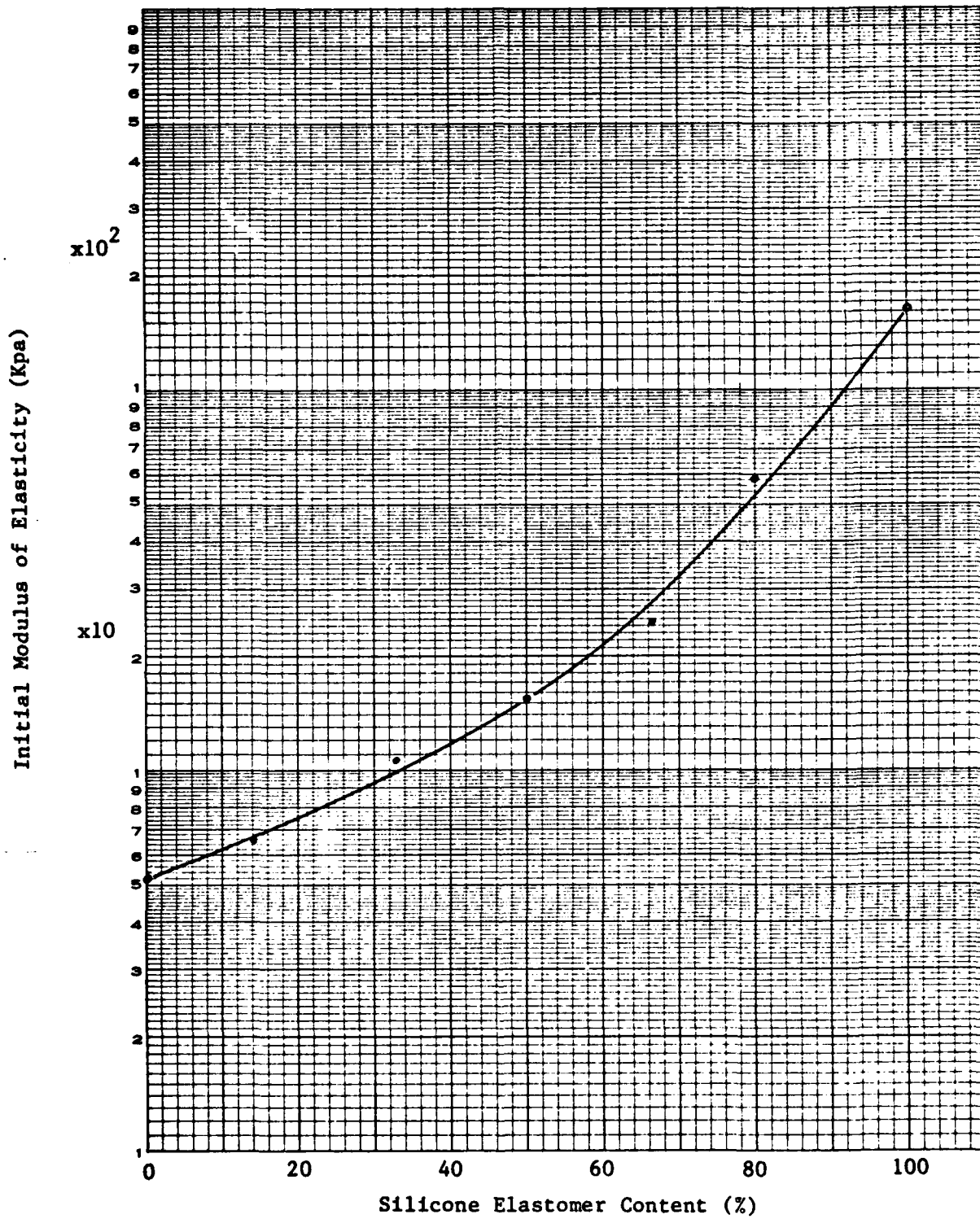[1] Emerson & Cumming, Inc.

[2] Dow Corning

FIGURE 6-3: COMPRESSIVE PROPERTIES OF MDX 4-4210
SILICONE ELASTOMER WITH VARIOUS LIQUID
FILLED CAPSULE LOADINGS.

The Q7-2218 gel would be an excellent binder and void filler for the capsules, however, the capsules inhibit the cure throughout the center portion of a composite. This is the reason for the very low modulus value of this composite.

The softest capsule composites are about as soft as some foams. The major difference between the two systems is that the volume of a foam decreases as it is compressed while a composite without air voids retains its same volume but changes its shape when compressed. In comparison, the tactile "feel" of a composite is probably more similar to the "feel" of flesh than of foam for this reason.

# 7. CONCLUSIONS

Capsules having an average diameter of 2.3 mm and a wall thickness of approximately 0.06 mm can now be produced repeatedly and in large quantities. Highly elastic shells are formed that will not rupture when the capsules are compressed to as much as one quarter of their original size. The capsules are compatible with many polymers and when loosely bonded together, form a mass that is as soft as some polymer foams.

Producing a composite to simulate the feel of skin over flesh requires a skin layer that is very soft. To achieve this softness, the films should be as thin as 0.20 to 0.25 mm. Under a skin layer of this thickness, the capsules can be felt as individual beads if they are not bound together. Therefore, it is recommended that a binder be used.

The capsules still tend to develop an indentation on aging. This may not be a disadvantage since it allows for closer packing of the capsules.

In the past, capsules were sometimes made that looked good when first made, but became hard or flaccid months later. It is not known how capsules from the recommended formulation will appear in six months' time.

At this stage of development, it is recommended that long term aging of capsules in a prosthetic-like pouch be tested. The test should include rough handling, washing and temperature changes. The results of the test would be based on the stability of resilence, size and shape of the pouch and the condition of its contents.

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