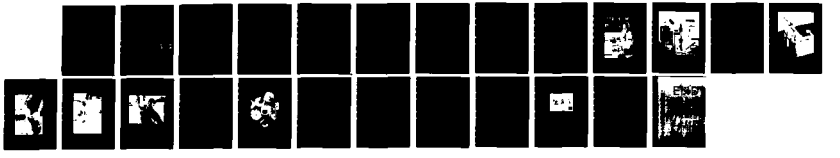
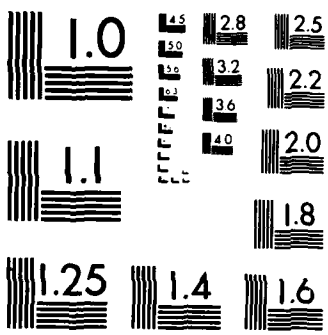
AD-A134 287 COMPOSITE MATERIALS FOR MAXILLOFACIAL PROSTHESES(U) 1/1
FRANKLIN RESEARCH CENTER PHILADELPHIA PA
R A ERB ET AL. AUG 79 FRC-A-C4842-2 DAMD17-77-C-7059
UNCLASSIFIED F/G 6/5 NL





AD _____

COMPOSITE MATERIALS FOR MAXILLOFACIAL PROSTHESES

Annual Progress Report

Robert A. Erb, Ph.D.
Stephen W. Osborn, Ph.D.
Harold L. Heller

AUGUST 1979

Supported by

U.S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
FORT DETRICK, FREDERICK, MARYLAND 21701

Contract No. DAMD 17-77-C-7059

Franklin Research Center
Division of The Franklin Institute
20th Street and The Parkway
Philadelphia, Pennsylvania 19103

Approved for public release; distribution unlimited.

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A134 287 / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Composite Materials for Maxillofacial Prostheses	5. TYPE OF REPORT & PERIOD COVERED Annual Progress Report 9 Aug. 1978 - 8 Aug. 1979
	6. PERFORMING ORG. REPORT NUMBER A-C4842-2
7. AUTHOR(s) Robert A. Erb, Ph.D. Stephen W. Osborn, Ph.D. Harold L. Heller	8. CONTRACT OR GRANT NUMBER(s) DAMD 17-77-C-7059
9. PERFORMING ORGANIZATION NAME AND ADDRESS Franklin Research Center 20th St. & Benjamin Franklin Parkway Philadelphia, PA 19103	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62775A 3S162775A825.AB.063
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Medical Research and Development Command, HQDA (SGRD-RMS) Fort Detrick, Frederick, Maryland 21701	12. REPORT DATE August 1979
	13. NUMBER OF PAGES 22 pages
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

MAXILLOFACIAL PROSTHESES; PROSTHETIC MATERIALS; MICROCAPSULES; SOFT FILLERS; ELASTOMER COMPOSITES

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The purpose of this program is to develop ultrasoft composite materials to be used as fillers in the fabrication of maxillofacial prostheses. The projected composite systems are elastomeric-shelled, liquid-filled microcapsules. Two experimental approaches were pursued toward making such microcapsules. One approach involves coaxial extrusion of a catalyzed elastomer precursor and core liquid into a receiving bath. The other approach involves interfacial (cont.)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

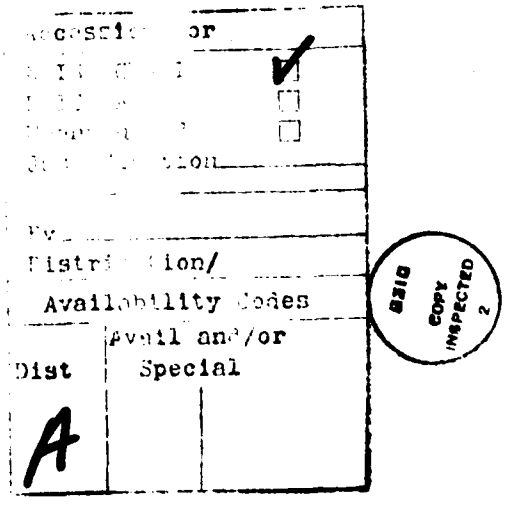
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. [cont.)

polymerization (e.g., of polyurethane) around droplets of core liquid suspended in a continuum containing reactive materials (e.g., diisocyanates).

ABSTRACT

The purpose of this program is to develop ultrasoft composite materials to be used as fillers in the fabrication of maxillofacial prostheses. The projected composite systems are elastomeric-shelled, liquid-filled microcapsules. Two experimental approaches were continued toward making such microcapsules. One approach involves coaxial extrusion of a catalyzed elastomer precursor and core liquid. Improvements added include: high-pressure flow-actuation system for shell components, variable-velocity carrier liquid, enclosed chopper, and non-aqueous collecting bath. Closed-shell capsules were obtained with the improved system. Further work is needed on increasing the volume fraction of liquid in the capsules. The other approach involves interfacial polymerization. Various reactive combinations to form polyurethanes and other materials were studied. A major problem has been to produce a wall which is elastomeric by a polymerization reaction fast enough to be practical. Closed-shell large diameter capsules have been obtained; improvements are needed in making smaller capsules and tougher walls.



FOREWORD

The concept behind this program is that a multiphase composite system should be able to simulate the mechanical properties of human soft tissue better than a homogeneous system could. The proposed composite of particular interest consists of liquid-filled, elastomeric-shelled microcapsules held together to form a deformable mass; this is to simulate the semi-liquid cellular structure of human soft tissue.

The second year's program has continued toward the goal of making suitable microcapsules. This task has proved to be considerably more difficult, and the systems and reactions more complex, than we had originally projected. Nevertheless, sealed, liquid-filled capsules have been obtained, and further advances in quality of product and production of larger quantities should permit study of the microcapsules in bonded structures.

CONTENTS

FIGURES

TABLE

1. INTRODUCTION

In the previous annual report the history of materials for maxillofacial prostheses was reviewed. Many materials have been used, but in recent times poly(vinyl chloride) plastisols, polyurethane compositions and silicones have been used effectively in simulation of skin and exteral features.

An area in particular in which further improvement is needed 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 lose internal liquid by syneresis).

This program is studying a new class of materials for use in fabricating maxillofacila 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.

2. MICROENCAPSULATION STUDIES

2.1 Experimental studies with coaxial extrusion

During this second-year program a new, high-pressure coaxial extrusion system was designed and fabricated. 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 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 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.

Experimental studies were carried out on stream-chopping methods. In the first-year program this was one of the areas of particular difficulty because of the viscous nature of the wall 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. In the early part of the second-year program 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. The liquid pulse cutoff method might be able to work, but would require a much more sophisticated system with a sonic variable-frequency generator, possibly square wave, impressed on a liquid stream passed through precisely positioned multiple ports.

A more effective method was found to be an enclosed rotating blade built into the extrusion head, which was totally redesigned. Figure 2 shows the new extrusion head. The elastomer-precursor and catalyst enter, unmixed, from their respective piston pumps. These materials flow

Figure 1. General view of coaxial extrusion system for forming liquid-filled, elastomeric-shelled microcapsules.

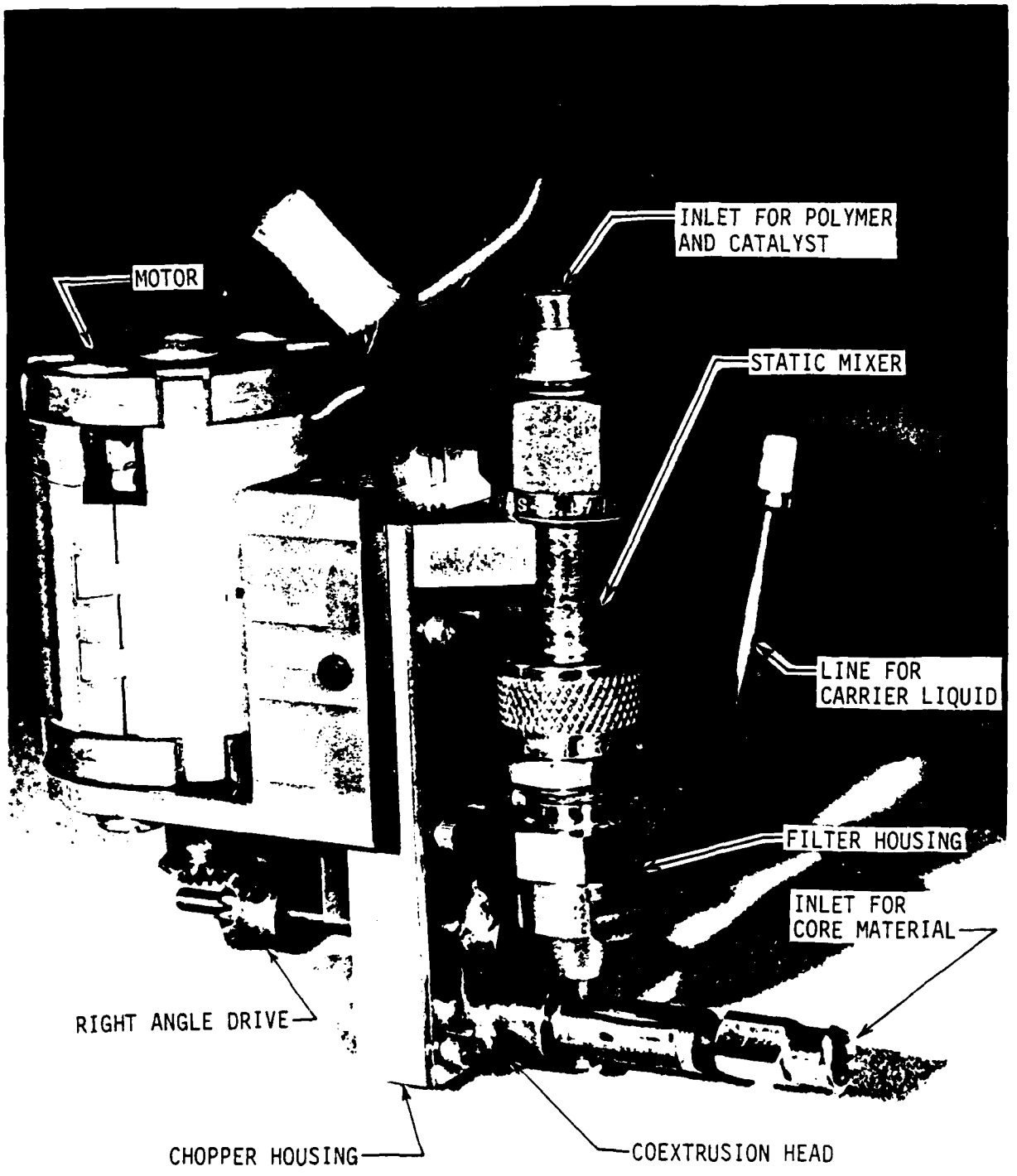


Figure 2. Extrusion head with enclosed chopper.

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, and the triple stream passed through the enclosed rotating chopper. Figure 3 shows the extrusion head assembly from another angle to show the orifice for the chopped stream

Figure 4 shows the carrier stream operating alone (without the coaxial stream and chopper for the illustration). The use of variable speed carrier stream has provided a useful added control on the capsule formation process. (The concept of a carrier stream at a higher velocity than the extrudate was originally set forth by G. R. Somerville of Southwest Research Institute.)

A further new development has been the use of a nonaqueous (vegetable oil) receiving bath and carrier stream. In the previous year's effort water and, later, graded-density aqueous salt solutions were used in the receiving bath. The problem with aqueous systems has been that a slight imperfection or incompleted closure in the unsolidified wall of the capsule will not heal but will 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 the vegetable oil (soy oil) for the bath, with proper adjustment of the operating parameters, has permitted capsules to close properly, with production of closed capsules approaching 100%. The oil is heated to accelerate the curing of the shell material.

Figure 5 shows microcapsules being formed. The oil in the receiving tank is agitated by means of a magnetic stirrer. This helps to prevent the formed capsules from agglomerating while they are still tacky. Figure 6 shows one of the series of fabricated mesh bags used to collect sequential samples of formed microcapsules during a run. The use of the collector bags permits samples to be taken from each of several parameter settings during a run. Comparison among the samples helps to define the optimum parameters fro the process. The overall parameters that can be varied, with some of these 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. 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 of weight

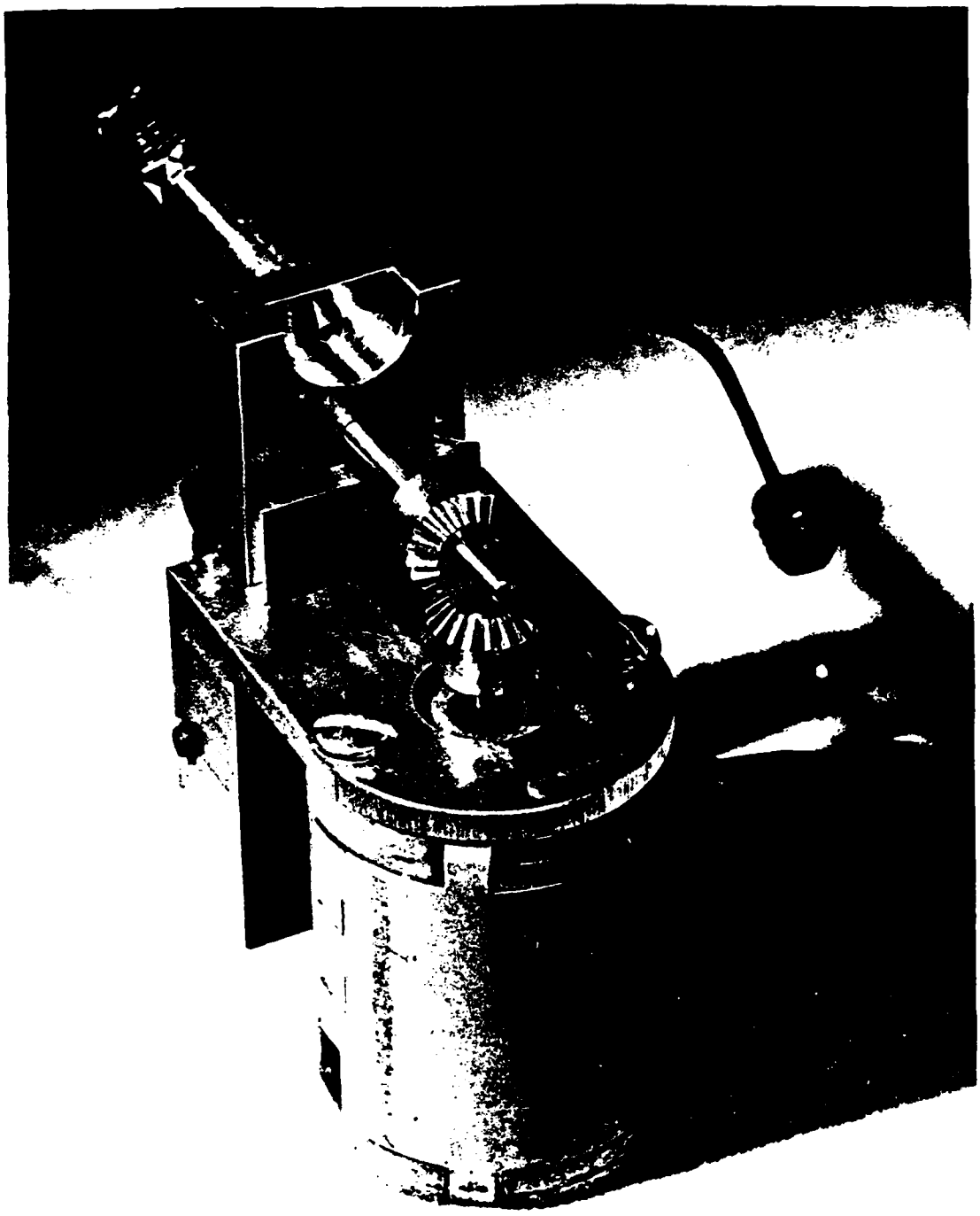


Figure 3. Extrusion head with enclosed chopper, showing orifice.

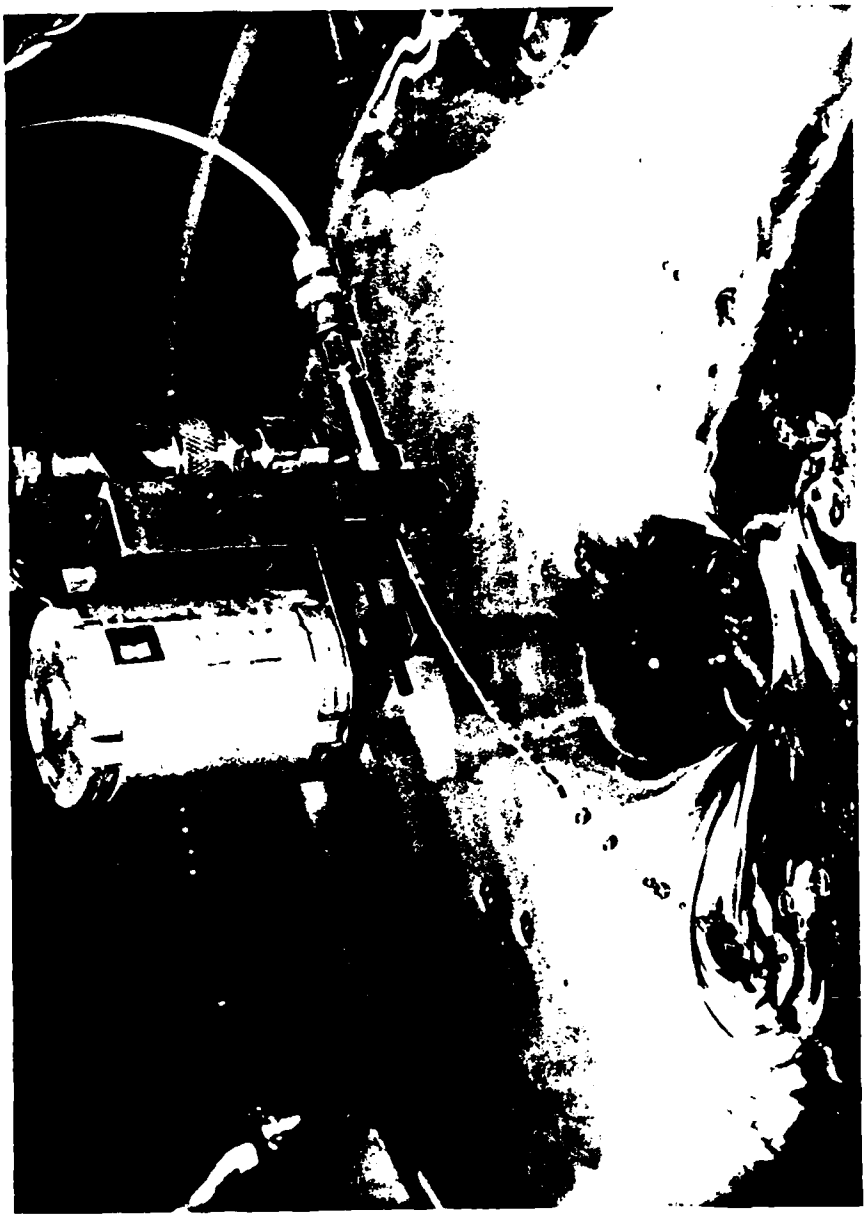


Figure 4. Carrier stream coming from extrusion head.

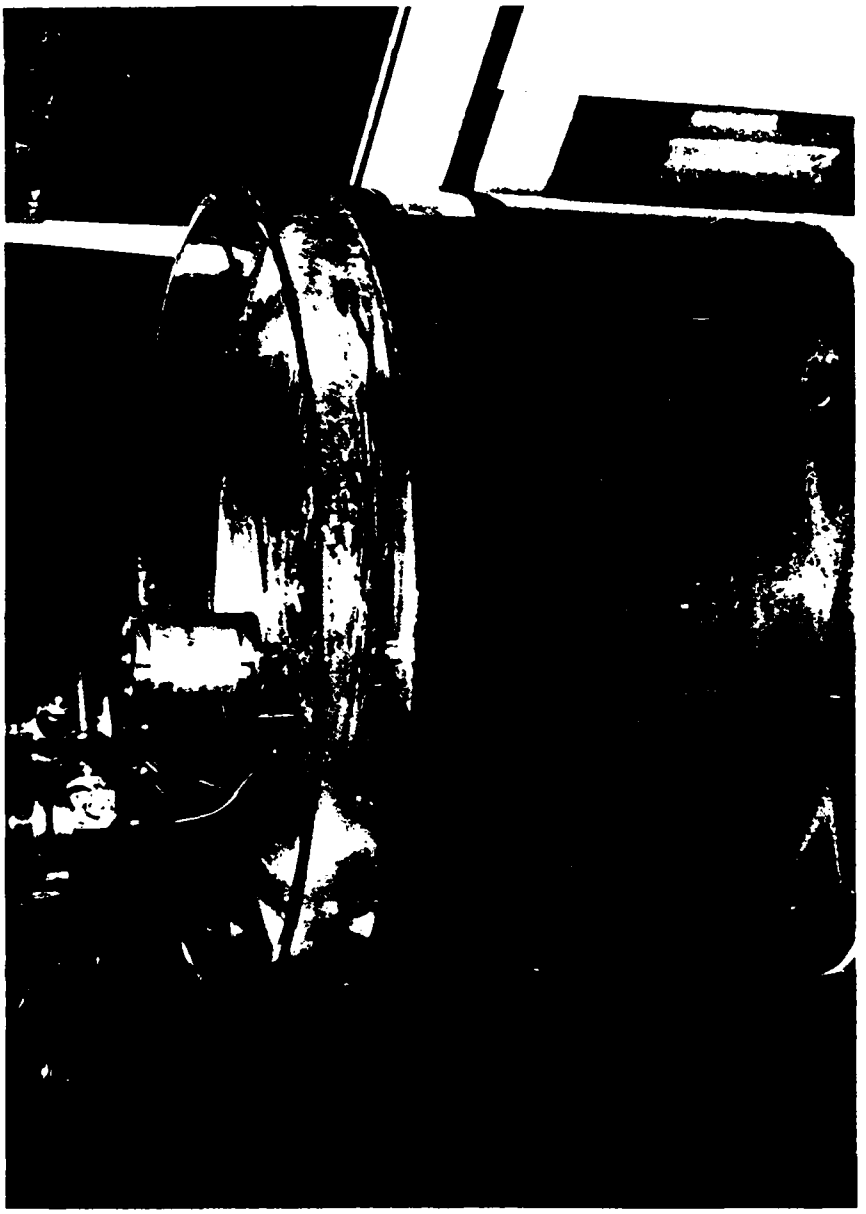


Figure 5. Microcapsules being formed.

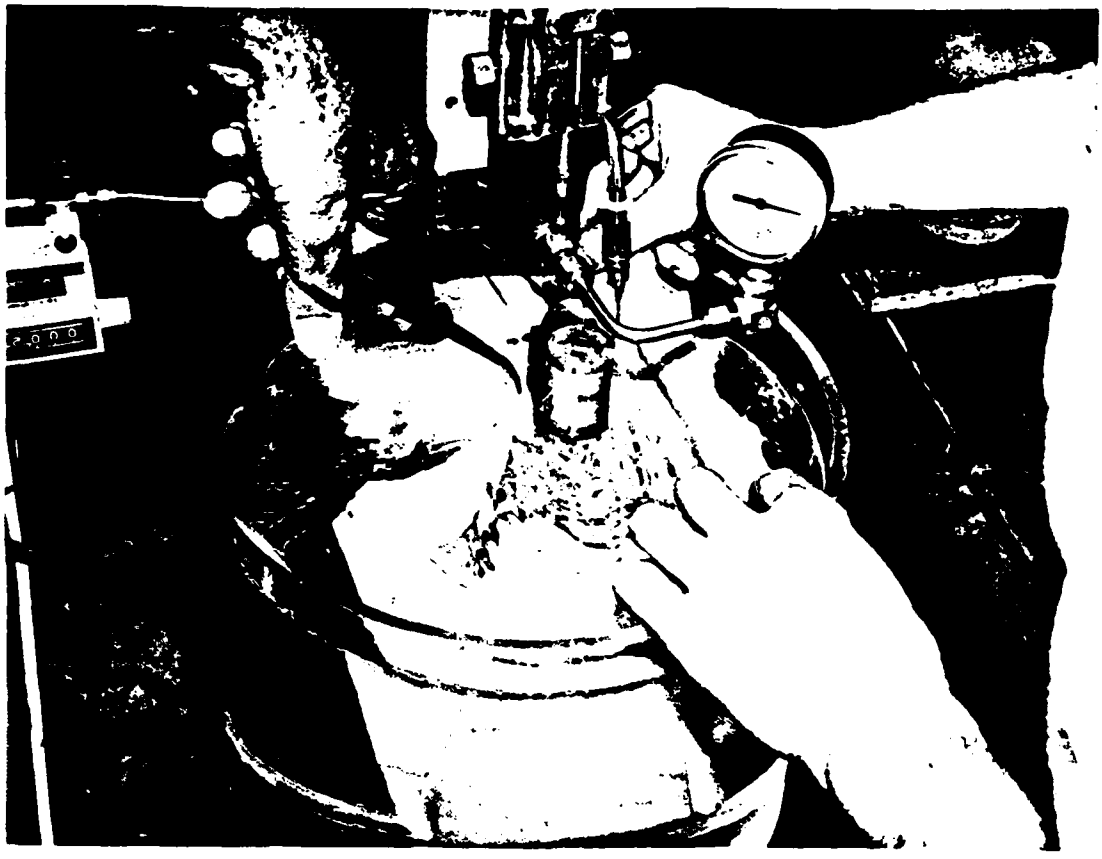


Figure 6. Use of mesh bag in collecting microcapsule samples.

pickup and swelling of Silastic 382 pieces in various core liquids (chosen from those listed in Table 1 of the previous annual report). The most satisfactory material tested was polypropylene glycol 4000. This was successfully substituted for the polypropylene glycol 1200 used in developing the first sealed capsules.

The capsules formed with Silastic 382 shells and polypropylene glycol 4000 cores do not show swelling or dimpling, and appear to have long term stability. Various microscopic techniques for examination of the microcapsules were studied. Most show only the outer shape; however, one method allows an undistorted view though the capsule wall. This involves immersion in and viewing through a layer of xylene. Figure 7 is a photomicrograph of closed, liquid-filled microcapsules approximately 1 mm in diameter. The most striking thing seen is the asymmetrical position of the cavity.

A technique was developed for making compressional stress-strain measurements on individual microcapsules. A digital electronic balance with 0.01 g sensitivity was used to measure stress. Displacement (strain) was measured with a micrometer-screw pusher. To compensate for movement of the balance's transducer a blank calibration curve was first determined.

Proposed further efforts in the coaxial extrusion program include: (1) improvements in the apparatus (replacement of the unreliable pump for the carrier stream, improving product collection means, arranging for a higher temperature bath, installing a bath cleaning system); (2) investigating a two-component, room-temperature-stable silicone material (Silastic 590) as a wall material; (3) studies to obtain improved geometrical characteristics with the microcapsules, particularly a higher volume fraction of contained liquid and better symmetry; (4) studies on how the geometrical characteristics relate to the effective moduli (or softness) of the capsules.

Also proposed is the bonding of produced microcapsules in elastomeric or gel matrices, and studying the mechanical properties of the combined system. Of particular interest will be the effect of the packing fraction of soft microcapsule filler on the properties of the final composite. Considerations and recommendations will be made as to which types of soft tissue might be effectively simulated with the microcapsule composites for maxillofacial applications.

2.2 Experimental studies with interfacial polymerization

In the interfacial polymerization part of the program, extensive experimental efforts were directed toward various reactive materials, the reaction parameters, and the resultant properties of formed shell material. A major problem has 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 are pinholes in the formed walls, cure-through to form solid spheres, and

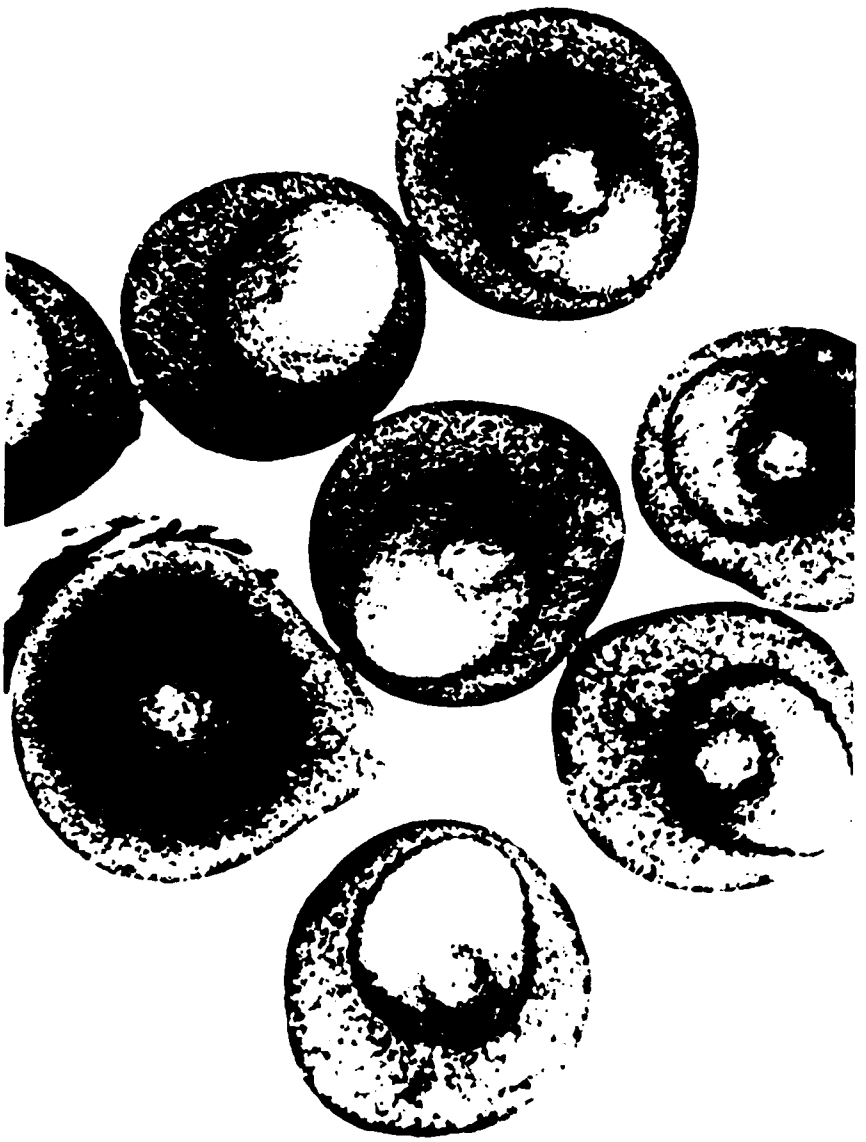


Figure 7. Microcapsules formed by the coaxial extrusion process.

agglomeration of formed capsules.

In attempting 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). Table 1 lists these combinations and the results. 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.

An interfacial liquid-drop method was used with diisocyanates in kerosene (constant or gradient 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 but with an unacceptably slow cure rate.

Studies were directed to a "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 under study toward improving the percentage of closed shells include adjustment of the acid chloride/polyol ratio and the use of various other amine curatives. Figure 8 shows capsules with closed shells with three different wall materials. As can be seen from the scale, the capsules are too large to be practical.

The emulsion process for making finer sized microcapsules, which was studied earlier in the program, is projected to be evaluated with the prepolymer systems which prove effective with the liquid-drop method. The liquid-drop method will also be modified in an attempt to make smaller capsules. Further development work is needed to define the reaction system more closely so as to maximize the mechanical strength, resiliency, and fluid retention ability of the walls. Characterization will be made of suitable microcapsules alone and in matrix systems.

Table 1. Polyurethane Shell Composition - Bulk Screening Tests

Run No.	Diols			Triols.			Tetrols		Amines		Catalyst	Isocyanates		
	PPG-4000[1]	P-2010[2]	P-410[1]	112-2[1]	TP-1540[2]	TP -4040[2]	PeP-450[2]	355[3]	1-7 Di-[4]	3,3'-Di-[5]	SnOctoate	TDI[6]	HyleneW[6]	
Eq.Wt.	2000	1000	212	~500	500	1367	100	124	65	44	-	87	131	Remarks
1		4.0							1.0				2.54	Immediate polymeriza-
2		2.5		1.5					1.0				2.68	tion to a friable,
3	2.0	2.0							1.0				2.38	wax-like solid - no
4		4.0								1.0			3.50	film formation -
5		2.5					1.5			1.0			4.42	extremely low tensile
6		2.5						1.5		1.0			3.88	strength
7		4.0					1.0			1.0			4.72	Rate of skin form-
8		4.0					1.0			0.5			3.27	ation decreased with
9		4.0					1.0			0.3			2.75	amine level
10		4.0					1.0			0.1			2.23	"
11		4.0					1.0			0.0			1.83	Very slow skinning
12		4.0						1.0		0.0			1.57	" " "

[1]Polypropylene glycol - diol. and triol. Dow Chemical Co.

[2]Polypropylene glycol - BAS Wyandotte

[3]PeP-450 containing a tert-amine catalyst

[4]1-7-Diaminoheptane Aldrich Chemical Co.

[5]3,3' Diaminodipropylamine Eastman

[6]DuPont Chemical Co.

Table 1. (cont'd) Polyurethane Shell Composition - Bulk Screening Tests

Run No.	Diols			Triols.					Amines		Catalyst	Isocyanates		
	PPG-4000	P-2010	P-410	112-2	TP-1540	TP-4040	PeP-450	355	1-7 Di-	33'-Di-	SnOctoate	TDI	HyleneW	
Eq.Wt.	2000	1000	212	~500	500	1367	100	124	65	44	-	87	131	Remarks
13		4.0					1.0			1.0		2.88		Rate of skin forma-
14		4.0					1.0			0.5		2.00		tion decreased with
15		4.0					1.0			0.3		1.68		amine level.
16		4.0					1.0			0.1		1.36		
17		4.0					1.0			0.0		1.12		
18		4.0					1.0			0.0	0.1	1.12		
19			4.0				1.0				0.1		3.80	Poor cures-brittle
20					10.0						0.1		2.62	Increasing hardness
21		8.0					1.2				0.1		2.62	through #23
22		4.0					1.6				0.1		2.62	
23		2.0					1.8				0.1		2.62	
24						11.0	1.2				0.1		2.62	Soft product
25		4.0					1.0				0.1	1.12		
26		6.0					0.8				0.1	1.12		Soft,yet tough product
27		8.0					0.6				0.1	1.12		Too soft
28		10.0					0.4				0.1	1.12		
29		12.0					0.2				0.1	1.12		
30		14.0					0.0				0.1	1.12		
31	8.0						1.0				0.1	1.12		Too soft
32	12.0						0.8				0.1	1.12		
33	16.0						0.6				0.1	1.12		
34	20.0						0.4				0.1	1.12		
35	24.0						0.2				0.1	1.12		
36	28.0						0.0				0.1	1.12		

Table 1. (cont'd) Polyurethane Shell Composition - Bulk Screening Tests

Run No.	Diols				Triols.		Tetrols		Amines		Catalyst	Isocyanates		
	PPG-4000	P-2010	P-410	112-2	TP-1540	TP-4040	PeP-450	355	1-7 Di-	33'-Di-	SnOctoate	TDI	HyleneW	
Eq.Wt.	2000	1000	212	~500	500	1367	100	124	65	44	-	87	131	Remarks
37		4.0						1.0			0.1	1.0		*Soft, tough product
38		6.0						0.8			0.1	1.0		#26 & 38 considered
39		8.0						0.6			0.1	1.0		best of series
40		10.0						0.4			0.1	1.0		Cure too slow for
41		12.0						0.2			0.1	1.0		efficient interfacial
42		14.0						0.0			0.1	1.0		cond.
43		6.0						0.8						1.0 Diethylaniline Some cure
44		6.0						0.8						0.5 " accel-
45		6.0						0.8						0.2 " eration
46		6.0						0.8						1.0 Tri-n-butylamine
47		6.0						0.8						0.5 "
48		6.0						0.8						0.2
49		6.0						0.8				1.0		
50		6.0						0.8			2 drops	1.0		Increasing cure rate
51		6.0						0.8			3	1.0		
52		6.0						0.8			4	1.0		
53		6.0						0.8			5	1.0		
54		6.0						0.8			6	1.0		
55		6.0						0.8		DAB CO	7 (Alg)	1.0		
56		6.0						0.8		33LV	0.05	1.0		
57		6.0						0.8		0.03	.05	1.0		
58		6.0						0.8		0.06	.05	1.0		
59		6.0						0.8		0.09	.05	1.0		
60		6.0						0.8		0.12	.05	1.0		
61		6.0						0.8		0.15	.05	1.0		Better but not fast

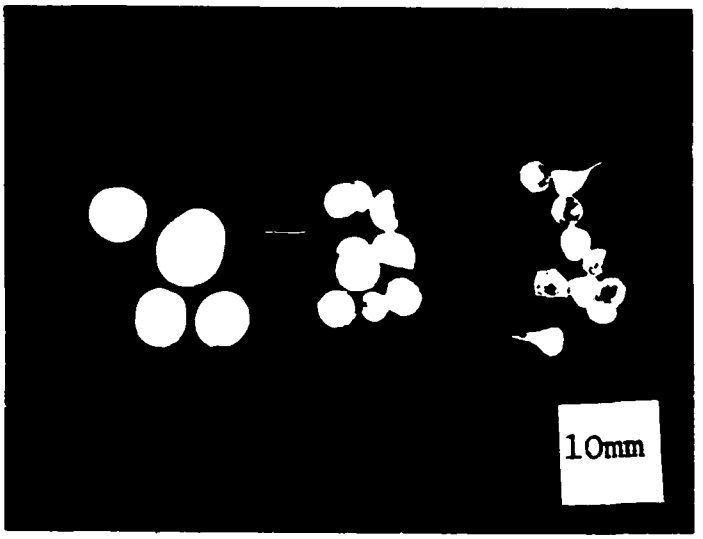


Figure 8. Capsules formed by the liquid-drop, interfacial polymerization process. Left to right: DIS-76-59-A, DIS-76-60-1, Dis-76-60-2.

4 copies	HQDA (SGRD-SI) Fort Detrick Frederick, MD. 21701
12 copies	Defense Documentation Center (DDC) ATTN: DDC-DCA Cameron Station Alexandria, Virginia 22314
1 copy	Dean School of Medicine Uniformed Services University of the Health Sciences 4301 Jones Bridge Road Bethesda, Maryland 20014
1 copy	Superintendent Academy of Health Sciences, US Army ATTN: AHS-COM Fort Sam Houston, Texas 78234

END

FILMED

11-83

DTIC