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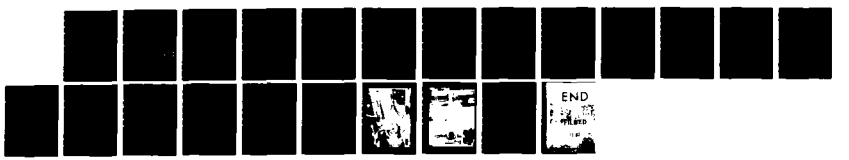

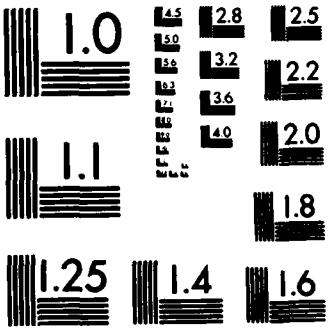

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COMPOSITE MATERIALS FOR MAXILLOFACIAL PROSTHESES

Annual Progress Report

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

November 1982

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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. Experiments continued on the interfacial polymerization process, with spherical sealed, capsules achieved. The diamine bath has been improved and an automatic system has been developed for producing the microcapsules. The one remaining parameter to be studied is the effects of various washing techniques on the freshly made microcapsules.

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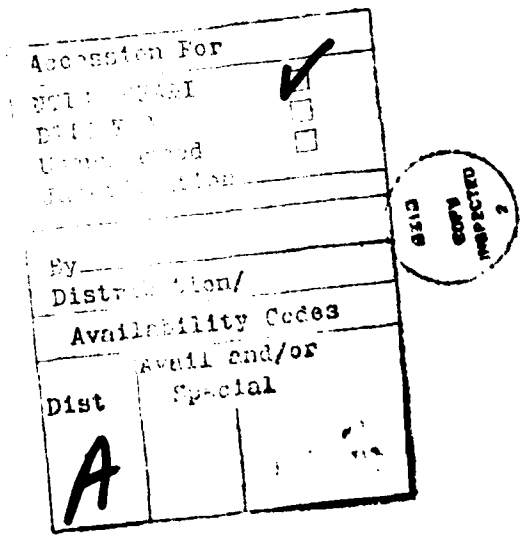

FOREWORD

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 fifth year's program has been directed toward the improvement of the diamine bath for higher production rates and continuous reproducibility of high quality microcapsules. An automated system for producing microcapsules was designed, built and tested and will be used for producing quantities of microcapsules for bulk testing. Attempts at improving the microcapsule shells has resulted in only minor improvements which indicate that the formulation is close to being optimum.

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).

This program is studying a new class of materials 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.

In the first 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 external features.

In the second annual report, efforts toward producing microcapsules by two experimental approaches were described. 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.

At the end of the second year, the coaxial extrusion approach was discontinued. The third annual report covers the further development of the interfacial polymerization process to the point where microcapsules could be produced.

In the fourth year it was realized that the amine type urethane catalyst inhibited the cure of silicone elastomers used as the matrix material for the microcapsules. In that year a successful switch was made to a non-inhibiting tin catalyst and small composite pieces were made. In that same year, processing parameters were being developed and have continued to be developed and used through this year.

During this report period various solvents, diamines and fumed silicas were evaluated for the bath. The optimum formulation for the microcapsules shells has been pursued and an automated system has been built and tested for producing the microcapsules.

2. DEVELOPMENT OF PRACTICAL TECHNIQUES FOR THE PREPARATION OF LIQUID-FILLED POLYURETHANE CAPSULES

2.1 SUMMARY

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

The new 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 appears to be readily adaptable to scaleup operations.

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 used at present for the maxillofacial prosthesis application 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. It is believed that all of the variables are now under control - up to the final washing of the microcapsules. The washing of the freshly made microcapsules does have an effect on their performance, and this will be looked into in the near future.

The curing time for the droplets in the diamine bath remains at two minutes as the standard, but shorter times are used in the automated production system. A study of bath solvents has shown that only a narrow range of solvents can be used, and the preferred diamine remains as 1,7 diaminoheptane.

The automated microcapsule production system has been built and tested and will be used for producing quantities of microcapsules for use in bulk systems.

2.2 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.

$$\underbrace{OCN\text{-}R^1\text{-}N{=}C{=}O}_{\text{Diisocyanate}} + \underbrace{H\text{-}O\text{-}R^2\text{-}OH}_{\text{Polyol}} \longrightarrow \underbrace{\{C\text{-}N\text{-}R^1\text{-}N\text{-}C\text{-}O\text{-}R^2\text{-}O\}}_{\text{Polyurethane}}$$

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.

$$\underbrace{-R^1NCO}_{\text{1/2 diisocyanate}} + \underbrace{N\text{-}R^3\text{-}NH_2}_{\text{Diamine}} \longrightarrow \underbrace{-R^1\text{-}\overset{H}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\overset{|}{N}}\text{-}R^3\text{-}}_{\text{Polyurea}}$$

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 continues for months.

2.3 MICROCAPSULE EXTERNAL PHASE

2.3.1 Bath Solvents

The diamine bath has so many restrictions on it that very little could be done over the last year to improve it. At this time, only minor improvements have been made. 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. A density of at least 1 gram per cubic centimeter
4. Easy wash-off from the microcapsules.

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 microcapsule materials.

A sensitive test was devised for determining swelling of the capsule shells, and is now applied to any solvents that are considered for use in the bath or as a rinse. Thi test co sts of spreading a thin film of the liquid

polymer on a metal surface and then dipping this into a diaminoheptane/kerosene bath to form a polyurea shell over a thin film of core material. This composite is then dipped into a test solvent for two minutes and then removed and examined for ripples. The large floating film attached at the sides is free to ripple if it expands, thus giving a clear indication of swelling.

A systematic approach for evaluating solvents is now in use. The core material and urethane mix are first checked for solubility in the solvent without the diamine. In the same solvent, a sheet of freshly prepared polyurea attached to a metal substrate (as described above) is checked for swelling after two minutes in it. If the first two tests prove satisfactory, diaminoheptane is added to a small volume of the solvent and stirred. A hazy appearance indicates poor solubility or reactivity. The table below lists the swelling properties of some common solvents on the polyurea shell material using the method described above.

Effect of Some Common Solvents on Microcapsule Shells

No Effect	Slight Swelling	Swelling	Soluble
Kerosene	Cyclohexane	Hexane	Alcohols
Exxon Isopar G	Octane	Toluene	Cellosolve
Exxon Varsol 1	Mineral Spirits	Freon TE	
		TCE	
		Acetone	
		Petroleum Ether	
		Heptane	

The few solvents that were found that could be used in the bath are quite similar. Kerosene with a boiling range of 190-261°C had been the preferred solvent up until recently. The microcapsules swell when left in it over five 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 over 30-40 microcapsules per cycle, the curing time needs to be increased, but returning to a slower rate (less microcapsules per cycle) the two minute cure in the same bath is satisfactory.

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 rate of 156-176°C. The diamine is more soluble in it, the Cab-O-Sil thickener disperses more easily in it and there is no problem with the shells swelling in it.

Earlier in the year, it was thought that petroleum ether and hexane satisfied 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 no longer interested in low boil solvents due to this problem and the swelling of the capsule shells, but they may find use as a quick rinse.

2.3.2 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.

Another Cab-O-Sil just now being explored is the hydrophobic grade N70-TS. This grade disperses quickly too, but gelling doesn't occur until about a half-hour later. This grade does not give the hazy appearance that

the M-5 does. The low amounts of Cab-O-Sil that are used is 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.

2.3.3 Diamines

In this year's work, 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.

2.4 INTERNAL PHASE

2.4.1 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. We are presently working with about

one percent triol. An increase in the trial 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 is 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.

DuPont has a series of polyether glycols that can be used to produce elastic urethanes. These Teracols were evaluated extensively for our use as linear chain polyols to replace the Pluracol P2010. The major difficulty found with this product was that only the 2000 molecular weight Teracol produced acceptable microcapsules, and due to its high viscosity, long tails were formed. Only fresh batches could be used since the viscosity of the

liquid polymer containued to increase as it aged. The viscosity of the Teracol having a molecular weight of 1000 was not low enough to yield any significant improvements, and furthermore, the polyurea shells produced by this grade were two fragile to handle. The use of the Teracols has been set aside and are not expected to be used in this program.

An interesting diisocyanate was found and evaluated as a possible replacement for the Desmodur W that we now use. It is an isophorone diisocyanate used for making clear urethane elastomers. In our process, it does not produce polyurea shells quickly enough, and therefore cannot be used.

At this point, our preferred formulation is as follows:

Materials	Percent
Diol P2010	71.75
Triol PeP 450	0.94
Diisocyanate (Desmodur W)	27.27
Stannous octoate	.04
	100.00

To the above formulation, the core material is added and allowed to stand for one day.

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

The present method used 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 now 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 ma' ial. 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.

Near the beginning of this year's work, it was noticed that the shelf life of the urethane formulations was increasing. The reason for this was not immediately apparent since good quality microcapsules could be made, but new formulations were found to be slow in reactivity and continued to have longer periods of shelf life. The viscosity of fresh duplicate batches was also lower than those made at an earlier date. It was found that the diisocyanate had degraded and had to be replaced. We requested a new can of diisocyanate from the manufacturer, but shipment was delayed for over a month due to a recall and repackaging of that product line.

2.4.2 Core Material

The core material now being used is Dow Polyglycol P2000. This product has worked well in the past and will continue to be used for this purpose. It was found earlier in the project 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.

We are now using 60% by weight of the core liquid rather than the 50% previously used. This has been done to reduce the shell thickness by reducing the urethane content. It appears that it might be possible to increase the core material content by at least another 10%. The benefits of this move is to reduce the viscosity of the mix and provide softer shells.

3. MICROCAPSULE PRODUCTION

The automated microcapsule making system has been built and tested. 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 the deep end and slowly settle to the belt, by which time sturdy shells are formed. A simple sketch of the system is shown in Figure 1.

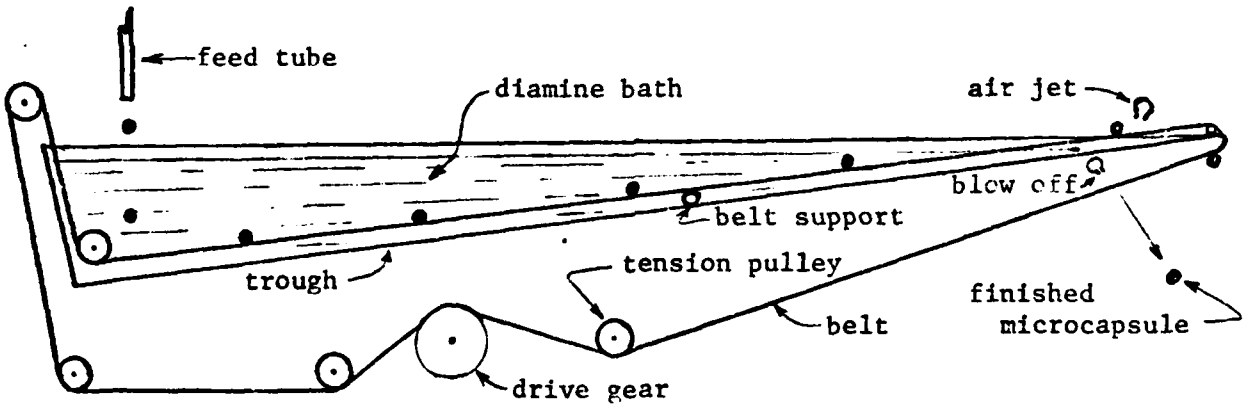

FIGURE 1. Diagram of Automatic Microcapsule Production System.

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 against the bottom of the trough, but it was found that the solvent was carried out over the top in the openings of the belt. A four mm diameter glass rod was mounted under the belt at the 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 microcapsules 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 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. A feed rate is selected that produces droplets with minimum tail formation. Figures 2 and 3 show the complete setup.

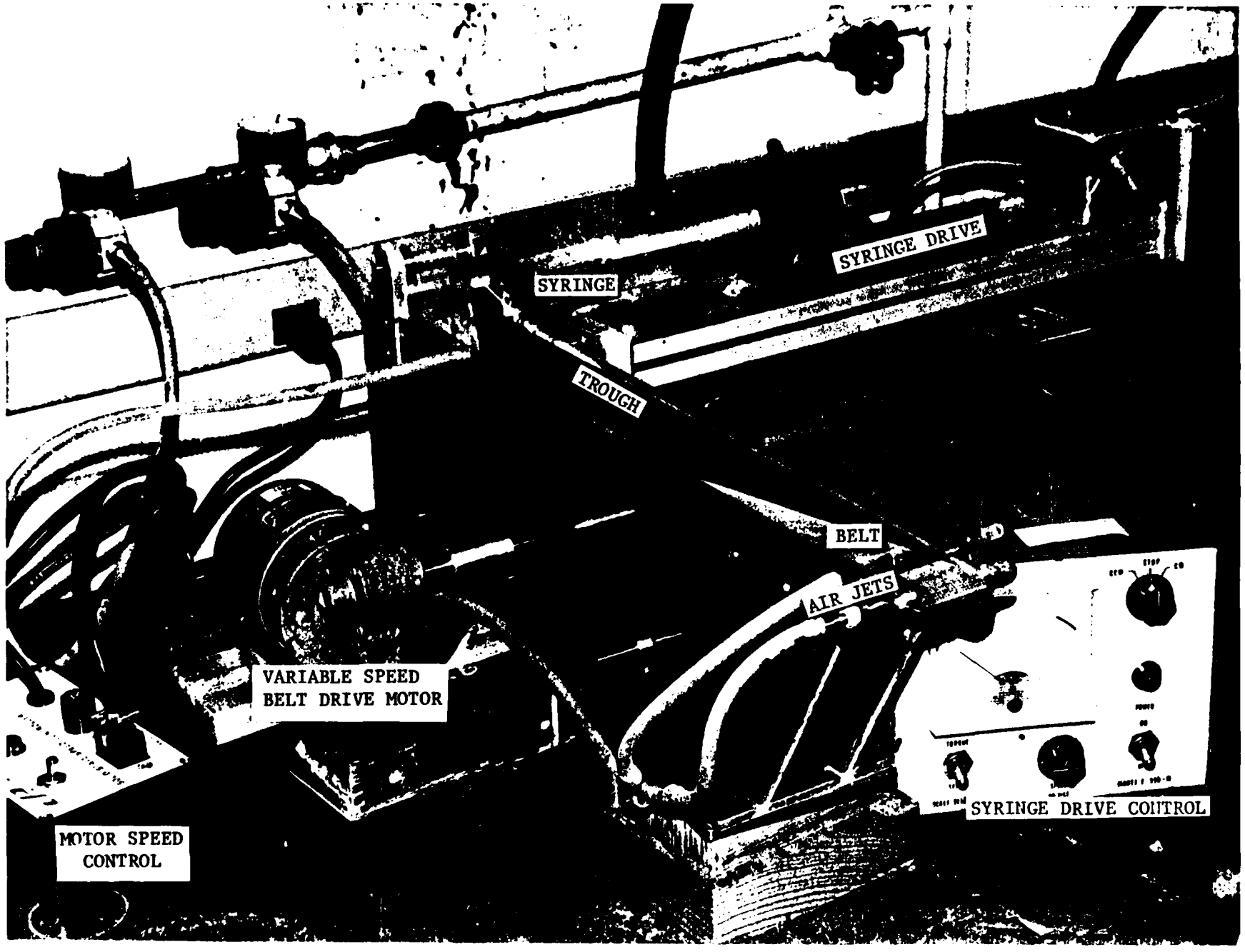

FIGURE 2. Automatic Microcapsule Production System.

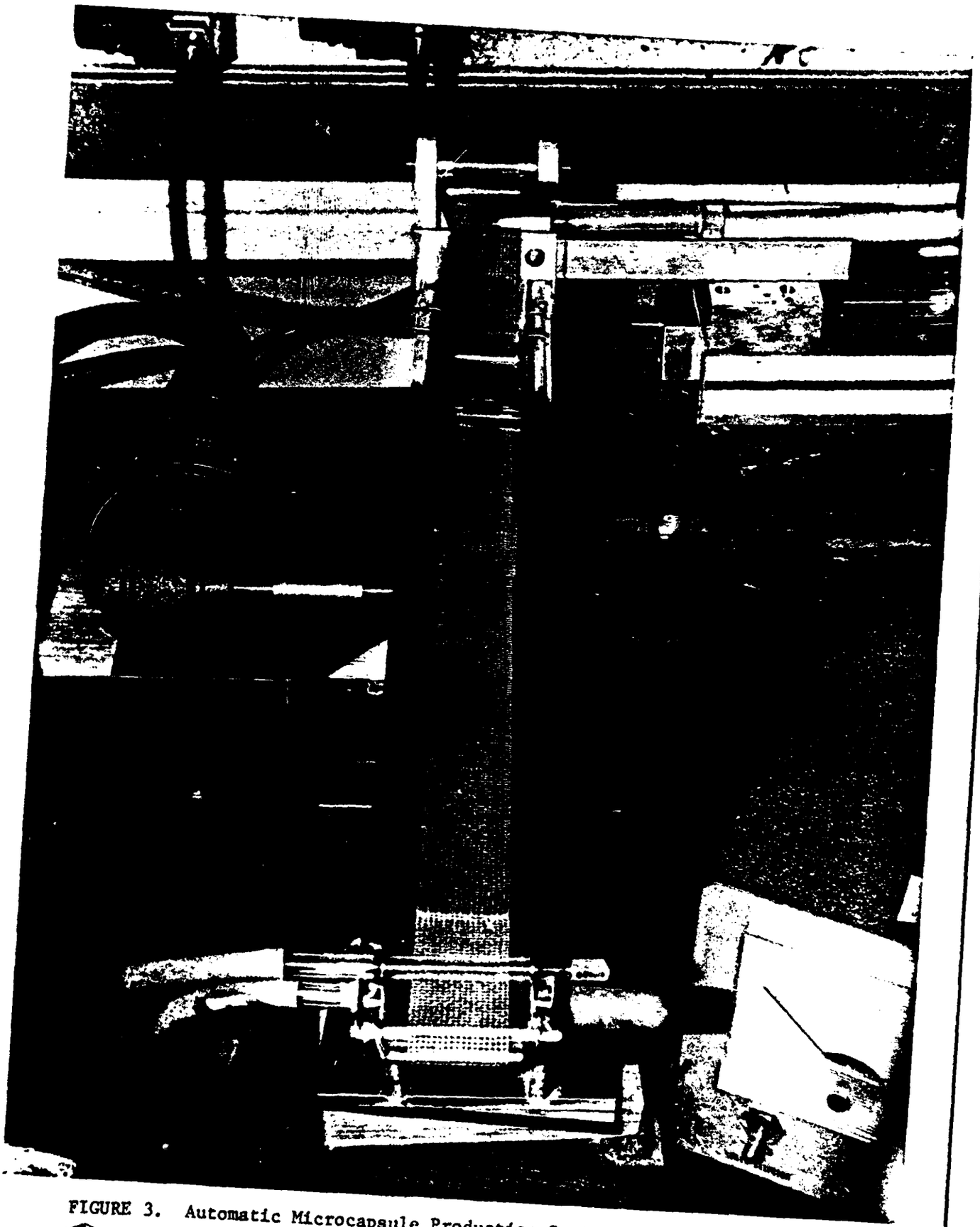

FIGURE 3. Automatic Microcapsule Production System (Trough Empty).

4. FUTURE PLANS

The emphasis in the final phase of this project will be directed towards the manufacture of microcapsules for use and testing as composite systems. These will be compared with foam and gel systems.

A washing procedure will be worked out for freshly made microcapsules. This is needed to remove the Cab-O-Sil, solvent and diamine from the capsules without shrinking or swelling them.

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