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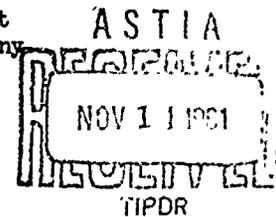
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Interim Report No. 3 (1 January, 1961 to 30 June, 1961)

A STUDY OF THE ENCAPSULATION APPLICABLE
TO LIQUID ROCKET FUEL

Paul Y. Hsieh
Fundamental Research Department
The National Cash Register Company

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Interim Report No. 3 on Contract No. NOnr2848(00)

Prepared By: Paul Y. Hsieh
Paul Y. Hsieh
Project Leader

Approved By: Philip D. Bouffard
Philip D. Bouffard, Head
Physical and Colloid Chemistry Section
Fundamental Research Department

Lowell Schleicher
Lowell Schleicher, Head
Fundamental Research Department

B. K. Green
B.K. Green
Manager of Chemical Research

G. J. Wilson
G. J. Wilson
Director of Research

FOREWORD

The following members of the Fundamental Research Department have cooperated in the research and the preparation of this report: Dr. Philip D. Bouffard, Section Head; Dr. Paul Y. Hsieh, Project Leader; Constantine C. Petropoulos, Research Chemist, James A. Herbig, (part time), and Harry L. Roe, Technician.

This report covers the work done from 1 January 1961 to 30 June, 1961.

INTRODUCTION

The research effort under the present contract is designed so that basic research may be conducted to study the phenomena related to encapsulation from non-aqueous media, with the long range objective of converting certain energetic, liquid fuels or oxidizers into "pseudo-solid", capsular products.

In past months, a major effort had been directed toward the attainment of a thorough understanding of the mechanism of polymer-film permeability. The results of this extensive study have provided us with a means of selecting, from the literature and/or from a minimum number of actual permeability measurements, candidate polymer materials to be used as capsular walls. Basic knowledge of permeability has also given us a means of determining possible chemical and/or physical alterations of capsular wall structures to meet the specific need of particular capsules. These have been reported previously (Interim Report No. 2).

After definite and significant advances had been achieved in the polymer permeability studies, and as a logical sequence thereof, the emphasis has been shifted to the second phase of this contract: the study of the phenomena involved in encapsulation from non-aqueous media.

The studies that have been conducted during present period are as follows:

1. Establishment of the essential conditions for the accumulation of macromolecules around a dispersed liquid droplet to be encapsulated (internal phase).
2. Encapsulation of liquids by interfacial polymerization approach.
3. Testing of the compatibility of ethylene diamine, 1,1-dimethyl hydrazine, and hydrazine with various solvents.

Previously, water was adopted as the model compound for encapsulation studies; however, during this period, amines, especially ethylene diamine, were selected as model compounds. The choice of ethylene diamine for the first step

of the proposed study is premised on the fact that this material approaches the character of the target substance, and because of a lower degree of reactivity, does not incorporate its hazards.

To summarize, the establishment of the prerequisites, especially the parameters introduced by interfacial free energies, for encapsulation in specific systems, along with the gradual emergence of study of the parameters for the stable dispersion of an I.r. in a non-aqueous system should complete the technology now lacking for the successful encapsulations of various liquids.

LIQUID ENCAPSULATION

I. Essential Conditions for an Encapsulating Material (Wall Material) to surround a Liquid to be Encapsulated (Internal Phase)

A. Theoretical Approach

The encapsulation now conducted at the National Cash Register Company is achieved by dispersion of the material to be encapsulated (internal phase or I.P.) into an immiscible supporting medium (dispersing medium) which contains polymers (encapsulating material) in a colloidal aggregate state. In order for the encapsulation to be successful, the encapsulating material must selectively deposit itself around the I.P. as a fluid mass, which is subsequently hardened by various techniques into a rigid film. This implies that the encapsulating material must have a greater affinity for the I.P. to be encapsulated than for other surfaces in its environment, i.e., the interfacial tension (interfacial energy) between the I.P. and the encapsulating phase must be greater than the interfacial tension between the I.P. and the dispersing medium. A relationship showing this can be derived by considering the free energy difference between successful and unsuccessful encapsulation as follows:

Let 1, 2, and 3 express the internal phase, encapsulating phase, and dispersing medium, respectively.

If 1 and 2 exist individually in 3, as shown in Figure 1, no encapsulation takes place, while if 1 is dispersed inside 2, and 2 in turn is dispersed in 3, as shown in Figure 2, there is encapsulation.

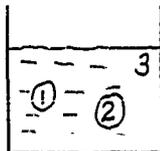


Figure 1

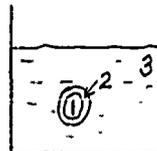


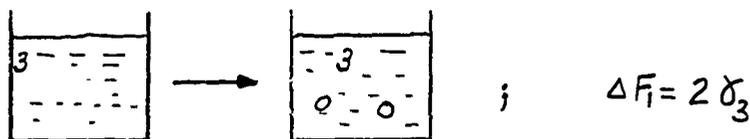
Figure 2

What is the difference in free energy between Figure 1 and Figure 2?

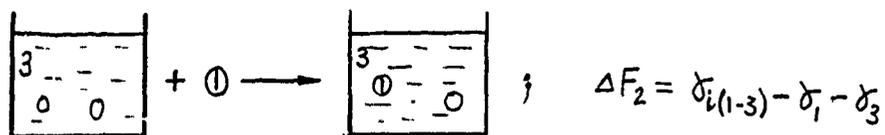
For better understanding of the situation involved the process can be considered stepwise, starting from and continuing to the final stages as shown in Figures 1 and 2.

The total free energy change involved in obtaining the state as shown in Figure 1 may be considered in three steps.

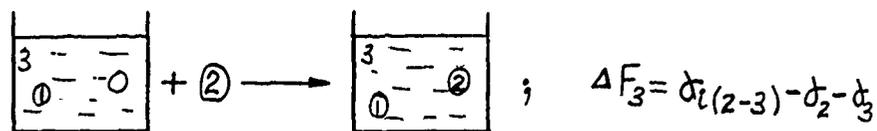
1. Create two holes of unit surface area inside 3 to accommodate 1 and 2. (σ = surface tension).



2. Put droplet 1 into one of the holes (σ_i = interfacial tension)



3. Fill the remaining hole with droplet 2.

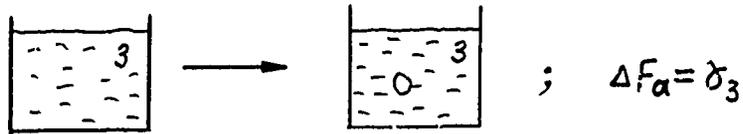


The total free energy change involved in no encapsulation, ΔF_N , is therefore the sum of the free energy change in each of these steps, namely,

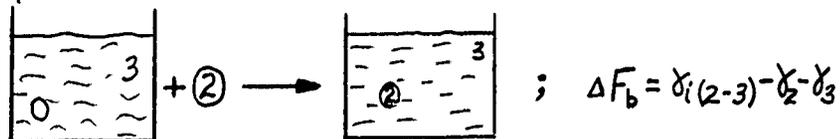
$$\Delta F_N = \Delta F_1 + \Delta F_2 + \Delta F_3 = \sigma_{i(1-3)} + \sigma_{i(2-3)} - \sigma_1 - \sigma_2 \quad (1)$$

The total free energy change in obtaining the state of successful encapsulation, as shown in Figure 2, can be considered in four steps.

1. Create a hole in 3 to accommodate droplet 2,



2. Fill the hole with droplet 2,



3. Create a hole inside 2 to accommodate droplet 1,



4. Place droplet 1 into the hole,



The total free energy change for a successful encapsulation, ΔF_y , is therefore the sum of each of these free energy changes:

$$\Delta F_y = \gamma_{i(1-2)} + \gamma_{i(2-3)} - \gamma_1 - \gamma_2 \quad (2)$$

The difference between successful and unsuccessful encapsulation is then the difference between equation (1) and (2):

$$\begin{aligned} \Delta F_y - \Delta F_n &= \gamma_{i(1-2)} + \gamma_{i(2-3)} - \gamma_1 - \gamma_2 - \gamma_{i(1-3)} - \gamma_{i(2-3)} + \gamma_1 + \gamma_2 \\ &= \gamma_{i(1-2)} - \gamma_{i(1-3)} \end{aligned}$$

Thus, the difference between successful and unsuccessful encapsulation is reduced to the difference of the interfacial tensions between the internal phase-encapsulating phase and the internal phase - dispersing medium.

The difference logically must be positive, and was confirmed by actual experiences described in the experimental section. It will be noted that the slight difference in the interfacial area between the system expressed in Figure 1 and that of Figure 2 has been omitted in the derivation for simplicity; this correction can be included, if necessary.

B. Experimental Approach

In the encapsulation process using The National Cash Register Company's gelatin system, it has been found that encapsulation of certain oils is "easy" in one system but "difficult" in another. Good examples are cassia (cinnamic aldehyde), castor oil, and Magna flux oil. Encapsulations of cassia and castor oil are "easy" in a 3 1/2-way¹ system but "difficult" in a 2-way² system, while encapsulation of Magna flux oil is "easy" in a 2-way system but "difficult" in a 3 1/2-way system; thus, they were considered to be the best choice for the study of the contribution of interfacial tension in "easy" and "difficult" encapsulation processes.

The results are shown in Table I.

Further interfacial tension measurements were carried out in the "Hot Melt System"³ a non-aqueous system, which was recently developed by The National Cash Register Company.

1. 2-way system-composed of 11.88 g. Gelatin, 11.88 g. gum arabic and 810 ml. water. Solution separates into two phases; a colloid rich (coacervate phase) and a colloid poor (equilibrium phase) at pH 4.5 and 40°C.
2. 3 1/2-way system-composed of 11.88 g. Gelatin, 11.88 g. gum arabic, 810 ml. water, 24 ml. 2% Ethylene-Maleic Anhydride-DX-840-21 and 24 ml. 2% Ethylene-Maleic Anhydride-DX-840-31. Solution separates into two phases; a colloid rich (coacervate phase) and a colloid poor (equilibrium phase) at pH 7.0 and 40°C.
3. Melt wax or other proper material to be used as wall material in a supporting medium which is inert to the material to be encapsulated. Internal phase is then dispersed in the hot melt mixture and after molten wax has built around the I.P. temperature is lowered to obtain a rigid wall. Silicone and fluoro. chemicals are often used as supporting media.

TABLE I
Interfacial Tension of Oils in a Gelatin Solution

Interface \ System	Interfacial Tension		dyne/cm. @40°C.	
	2-Way	Encapsulation	3 1/2-way	Encapsulation
Cassia - Coacervate phase	2.1	hard	19.4	easy
Cassia - Equilibrium phase	9.0		7.7	
Castor Oil - Coacervate phase	10.8		12.7	
Castor Oil - Equilibrium phase	12.7	hard	11.8	easy
MFO - Coacervate phase	18.5	easy	29.0	hard
MFO - Equilibrium phase	7.0	..	36.8	

MFO: - Magnaflox oil

There has been some success in the encapsulation of toluene diisocyanate (T.D.I.) and diethylene triamine (DETA) using this system, therefore, the interfacial tensions between these materials and molten paraffin wax and a supporting medium, FC-43 (Minnesota Mining and Manufacturing Co.), were determined and results are shown in Table II.

C. Discussion

The data shown in Tables I and II were obtained by means of a Du Noüy ring-type tensiometer, which although accurate results cannot be expected, has enabled us to establish a general trend. Refined data will be secured by a pendant drop apparatus now in operation.

From the tables and from the encapsulation experiences, it can be concluded that for the encapsulation to be successful the internal phase-encapsulating phase interfacial tension must be greater than the internal phase-equilibrium (or supporting) phase interfacial tension. The essential point might be the magnitude of the difference rather than the actual magnitude of the interfacial tension itself.

If this is one of the essential conditions, then the determination of interfacial tension would be a guide in choosing the right system for the encapsulation of a given liquid.

TABLE II

Interfacial Tension in the "Hot Melt System"

Interfacial Tension @55°C

TDI - paraffin	0.7
TDI - FC-43	5.0
DETA - paraffin	8.8
DETA - FC-43	2.6



Pendant drop apparatus

II. Interfacial Polymerization Encapsulation of Liquids

A. Theoretical Approach

In principle, encapsulation is possible, if a rigid-film-forming reaction can be engineered to take place just at the interface between an I.P. and a supporting liquid. The following processes may be applicable.

1. Disperse the I.P. into a supporting medium containing monomer, in the form of droplets. Induce the polymerization reaction by incorporating a catalyst into the I.P. before dispersion or by irradiating it with U.V. light.

2. Dissolve one of the reactants in the I.P. and dissolve another in the supporting medium. Co-polymerization can then be carried out at the interface by bringing the two solutions into contact or by exciting the reactants with some energy source.

3. Utilize the high reactivity of the candidate internal phases (I.P.) itself and let it react with a polymer at the interface.

Since these approaches involve more components, the compatibilities of the components must be carefully studied in order to obtain a workable system.

Previous attempts along these lines were unsuccessful, largely because the particular I.P. was kept dispersed as small droplets entirely by mechanical agitation. This resulted in a dynamic, rather than a static dispersal wherein the individual droplets continually coalesced or flocculated and were reformed. Since the attempted reactions usually require a finite time, continuous coating could not be achieved with a continually changing interface.

Without specific knowledge concerning the factors governing stable dispersions of "oil-in-oil" systems, interfacial polymerization has been studied by stationary contact of two immiscible phases or by dropping the heavier phase into the lighter phase as single droplets without mechanical agitation.

B. Experimental Approach

The exploratory work has been done mostly to study the applicability of interfacial polycondensations in the encapsulation of diamines.¹⁻¹¹

Example 1. Water encapsulation

An aqueous solution of 1,6-hexane diamine (0.4 mole/liter) was dropped slowly into a solution of sebacyl chloride in carbon tetrachloride or n-hexane (0.06 mole/liter). A thin, tacky film formed instantly around the water, but the water capsules so produced were not rigid enough for easy handling. By further coating these capsules with paraffin wax in the "Hot Melt System", it was possible to protect the I.P. for about two weeks.

Example 2. Hydrazine encapsulation

Hydrazine was injected into a solution of sebacyl chloride in carbon tetrachloride (0.06 mole/liter). An extremely rapid reaction took place; however, a protective film did not form due to the low molecular weight of the condensation product.

Example 3. Ethylene diamine encapsulation

Ethylene diamine was dropped into 200 ml. of n-hexane containing 3 g. sebacyl chloride. A rapid polymerization resulted in the formation of a clear, transparent, fragile wall around the ethylene diamine droplet; however, due to permeation the wall was insufficient for the protection of the I.P. for a prolonged period.

Further studies were carried out with the various film-forming reactions, at stationary interfaces as described previously. The following combinations have shown rigid film formation at interfaces.

Epoxy resin (Epon 820 and 828, Shell Oil Co.)	- Tributyl amine
"	- Polyamine resin/heptane
"	- N-methyl morpholine
"	- Triethylamine/heptane
"	- Toluene diisocyanate
Polyether (G-2410, Atlas Powder Co.)	- Toluene diisocyanate
Ethylenediamine	- Toluene diisocyanate

Tetraethylene glycol dimethyl metacrylate polymerizes within twenty seconds when irradiated by U.V. light, in the presence of the initiator benzoin methyl ether. The polymerization product is very tough and transparent. This type of polymerization could provide a potentially workable system and deserves further study.

C. Discussion

There are at least two factors involved in the problem concerning the surrounding of an I.P. with a polymer wall which should be considered before any encapsulation techniques by interfacial polymerization are attempted. They are the speed and ease of polymerization and the permeability of the polymeric material to the internal phase.

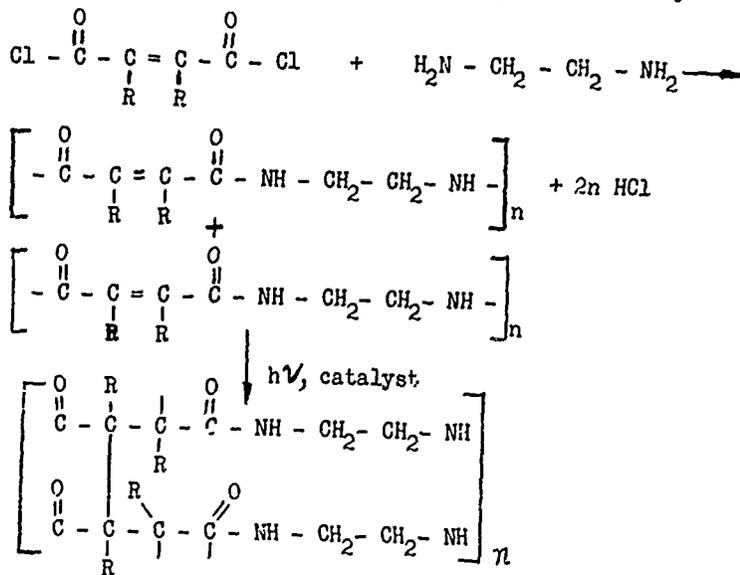
Encapsulation by interfacial polymerization requires an easy and fast reaction; however, the resulting film usually has a high permeability to polar molecules due to the polar nature of the polymer produced. On the other hand, vinyl-type addition polymers have a low permeability to polar molecules due to the hydrocarbon-type skeleton. The polymers, however, are usually formed at high temperature and at high pressure in some cases. Long reaction times as

well as severe reaction conditions make direct application of this type of reaction difficult in encapsulation processes.

Three approaches can be considered.

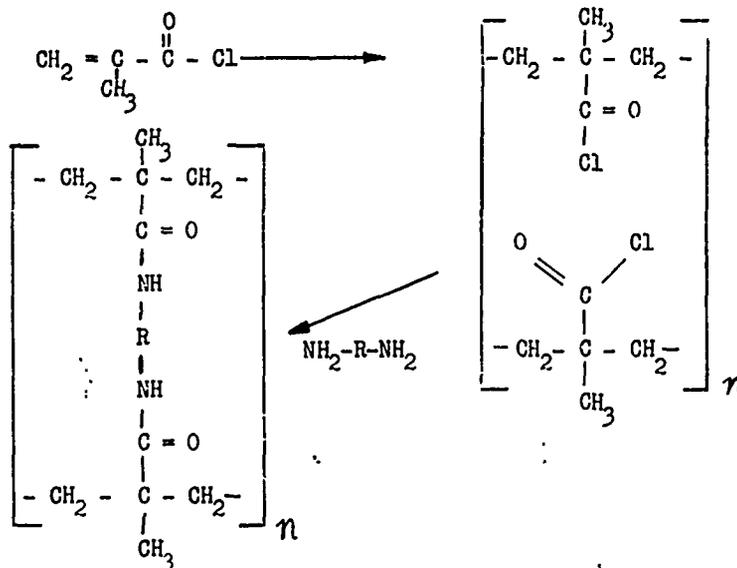
1. Use of interfacial condensation polymers to provide temporary protection and to facilitate further handlings. Final protection is then achieved by the introduction of a second hydrocarbon-type polymeric wall, by addition polymerization techniques.

2. Formation of a temporary skin which contains some unsaturation by interfacial polymerization techniques. The unsaturated groups are subsequently crosslinked to obtain a film of good quality. For example, unsaturated diacid chloride and a diamine may be polymerized by interfacial condensation utilizing their fast reaction to form a temporary skin around an internal phase. The unsaturated bonds are then crosslinked photochemically.



3. Utilization of a vinyl-type condensation polymer with reactive groups on the side chain and then cross linking, if necessary, by condensation polymerization.

For example:



4. Attainment of a good impermeable capsular wall in one step at reasonable speeds of polymerization without using severe reaction conditions. This might be accomplished through photopolymerization.

According to the tests conducted at Britain's Atomic Energy Research Establishment at Harwell on the permeability of half a dozen commonly used plastics (nylon, acrylic, polystyrene, polyvinyltoluene, polyethylene and a fluorocarbon), nylon was found to be the least permeable material. (Product Engineering p.9, December 19, 1960). This implies that the current interfacial polymerizations which form polyamides may have some useful applications.

III. Compatibility Studies

Whichever encapsulation process - phase separation, "Hot Melt Method", interfacial polymerization, mechanical method, etc. - is to be used, knowledge of the compatibilities of the materials to be encapsulated with the other organic liquids to be used is important in the selection of the right workable system. Extensive miscibility tests were conducted on ethylene diamine, 1,1-dimethyl hydrazine, and hydrazine, and the significant results are listed in Table III.

A great similarity in the properties of ethylenediamine and hydrazine may be noticed. The similarities of the model compounds to the target substance are summarized, in part, in Table IV.

TABLE III

Miscibility of Three Amine Compounds (25° C)

	<u>Ethylenediamine</u>	<u>1,1-Dimethylhydrazine</u>	<u>Hydrazine</u>
1-Bromodecane	I	R	I
n-Hexadecane	I	M	I
2-Octanone	I	M	I
n-Butyl Ether	I	M	I
Cyclohexane	I	M	I
Deobase	I	M	I
JP-4	I	M	I
Triethyl Benzene	I	M	I
Mesitylene	I	M	I
1,2,3-Trichloropropane	I	M	I
2,2,4-Trimethylpropane	I	M	I
Cis-Decahydronaphthalene	I	M	I
n-Amylether	I	M	I
n-Hexylether	I	M	I
Triethyl Amine	I	M	I
Diocyl Phthalate	I	M	I
Iso-Decyl Phthalate	I	M	I
Santicizer 214	I	M	I
Santicizer 213	I	M	R
Cumene	I	M	I
n-Heptane	I	M	I
n-Hexane	I	M	I
n-Deçane	I	M	I
n-Dodecane	I	M	I
n-Octane	I	M	I
n-Tetradecane	I	M	I
1,2-Dimethyl Cyclohexane	I	M	I
Petroleum Ether	I	M	I
Petroleum Naphtha	I	M	I
Dichloromethane	I	M	I
Phenylcyclohexane	I	M	I
Bromoform	I	M	I
Amyl Biphenyl	I	I?	I
Tetrahydronaphthalene	I	M	I
Methyl Vinyl Ketone	I	M	I
Methyl Nonyl Ketone	I	I?	I
1-Bromo-3 Methyl Butane	I	R	I
Tetraethylene Pentamine	I	M	M

I = Immiscible

I?=Possible Reaction

R = Reaction

M = Miscible

TABLE IV

Property Data for Ethylenediamine, 1,1-Dimethylhydrazine & Hydrazine

	<u>Ethylenediamine</u>	<u>1,1-Dimethylhydrazine</u>	<u>Hydrazine</u>
Molecular Weight	60.0	60	32.
Melting Point, °C.	8.5		1.4
Boiling Point, °C.	117.2		113.5
Density, g/cc	0.899	0.791	1.011
Heat of Vaporization, K-cal/M.	10.7		11.2
Flash Point, C.	33.9		52.2
Surface Tension, Dyne/cm			66.7
Refractive Index	1.4540 ^{26°}	1.4075 ^{22.3°}	1.4644 ^{35°}
Vapor Density	2.07		1.1
Viscosity, CPS @25°C.	1.725		0.90
Vapor Pressure, MM of Hg @25°C.	10.0		10.4
Heat of Fusion, Cal/Mole	4600.0 ^{15°}		3025.0 ^{25°}
Heat of Solution, Cal/Mole	7.6		1800.
Heat of Combustion, Cal/Mole	452.6		148,600.

IV. Plans For The Future

No matter which encapsulation method, phase separation, the "Hot Melt Method", interfacial polymerization, etc., is utilized, successful encapsulation requires the dispersion, with agitation, of a liquid internal phase in the form of droplets for a certain length of time.

Coalescence, reformation, and agglomeration have been a problem in attempts to encapsulate liquids by any promising method. It is felt that this dominating problem of obtaining stable dispersions of "oil-in-oil", a problem which is common to various potential methods of encapsulation deserves extensive study in the area of investigation now in progress.

Variables requiring definition include the droplet size, the droplet size distribution and the droplet concentration, as well as other interfacial parameters. The application of surface active agents could possibly alleviate the difficulties.

The literature is well documented with such studies in oil-water systems; however, little work has been done in non-aqueous "oil-in-oil" systems which have been of concern to us.

In the preparation of water-oil and oil-water disperions, the hydrophile-lipophile balance scale is chosen as a guide. It is felt that a similar approach can be used in the oil-oil system. The pendant drop apparatus (Fig. 3) can be used to advantage in this area. A better understanding of the role played by a surfactant in an oil-oil system would represent a major step toward the successful encapsulation of liquid fuels.

The pendant drop method of studying interfacial phenomena is superior to the various dynamic methods. The above statement is based on the fact that the static approach employed by the pendant drop method does not disturb the surface during measurement. This is especially important in the study of the change in interfacial tension with time.

Before moving into hydrophile-lipophile balance area, the apparatus would be used to obtain better data in the system described in section I. Conclusions secured from these measurements could then be used as a guide to obtain and establish a workable system for the target compounds.

With this information, once it is available, actual encapsulation of model amines will be carried out by the "Hot Melt Method" which has shown great promise.

The interfacial polymerization approach will be pursued along the lines discussed in Section II C. It is to be stressed especially in the area of film permeability with broadened emphasis on possible ways and means of altering and improving the permeability characteristics of specific polymer systems.

It is believed that by integrating the knowledge acquired up to this time and that to be obtained, the encapsulation of high energetic liquids will become a reality in the near future.

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