

STATISTICAL APPROACH TO COMMON VARIABLES IN EMULSION PREPARATION

By F. R. BENSON, W. C. GRIFFIN, and H. M. TRUAX*

Presented May 8, 1962, New York City

IT HAS been long known that the type and stability of an emulsion formed from a given oil-emulsifier combination are related in part to method of preparation. Techniques which are more or less generally applicable to the formation of stable o/w and w/o emulsions are described in treatises on emulsion technology (1, 5). Thus it is frequent practice to add the oil to a solution of the emulsifier in water in order to obtain a stable o/w emulsion. Similarly a usual procedure for preparing a w/o emulsion is to add water to an oil solution of the emulsifier. In the inversion technique an initially formed w/o emulsion is inverted to an o/w emulsion by the addition of further quantities of water. Except in the instance of inversion techniques, vigorous dispersion, such as that obtained with a colloid mill, usually generates finer particles and therefore more stable emulsions than does propeller stirring. It is usually considered that the greater the amount of proper emulsifier the more stable will be the resulting emulsion. Relative quantities of internal and external phases also contribute to stability; although there are exceptions, the internal phase in stable emulsions usually does not exceed 70 per cent. For different oils and emulsifiers, however, the validity of these considerations, which are part of the art and theory of emulsion technology, is not always certain, nor is the relative importance of these preparational variables capable of direct deduction. The investigation reported herein was undertaken to determine the importance of these common preparative variables on the type and stability of emulsions of water and different nonaqueous liquids with a series of surfactants.

In the present study, the importance of six preparative variables has been investigated by means of a statistically designed experiment. In this type of experiment, several factors are varied simultaneously according to a systematic plan, thereby enabling screening of the importance of each variable with an appreciably smaller number of experiments than would be required if each factor were varied one at a time. A fractional, two-level

* Atlas Chemical Industries, Inc., Wilmington 99, Del.

factorial design (4) was used to screen the following factors at the indicated levels:

	Levels	
Order of addition	o → w	w → o
Emulsifier location	w	o
Emulsifier concentration, %	1	2.5
Proportion of water, %	90	30
Temperature, °C.	25	70
Agitation	Propeller	Homo-Mixer*

* Trademark of Eppenbach, Inc.

Each preparation factor was studied at two values or procedural conditions except the proportion of water, which was investigated at three levels. Although for each emulsifier-oil pair there are 96 combinations, only twelve separate experiments in this design are required to screen the importance of the six factors. The twelve methods are indicated in Table 1.

TABLE 1—EXPERIMENTAL DESIGN OF EMULSION PREPARATIVE VARIABLES STUDY

Method Number	Order of Addition	Emulsifier Location	Emulsifier Conc., %	Water, %	Temp., °C.	Agitation Method
1	o-w	w	1	90	25	Propeller
2	w-o	w	2.5	90	70	Propeller
3	o-w	o	1	30	70	Propeller
4	w-o	o	2.5	30	25	Propeller
5	o-w	o	1	50	70	Propeller
6	w-o	w	1	30	25	Homo-Mixer
7	o-w	w	2.5	30	70	Homo-Mixer
8	w-o	o	2.5	50	25	Propeller
9	o-w	w	2.5	50	70	Homo-Mixer
10	w-o	w	1	50	25	Homo-Mixer
11	w-o	o	1	90	70	Homo-Mixer
12	o-w	o	2.5	90	25	Homo-Mixer

In the experimental design, as shown in Table 1, the experiments may be divided into three groups of four methods each according to the proportion of water used. Thus methods 1, 2, 11 and 12 utilize 90 per cent water, methods 5, 8, 9 and 10 utilize 50 per cent water and methods 3, 4, 6 and 7 employ 30 per cent water. Comparisons for each of the variables are made with two of these groups of four experiments at a time. For convenience, these combinations of groups are designated in this article by the quantity of water in the groups under comparison as 90-30 or 90-50. The nature of the present experimental design is such that valid comparisons may be made within the 90-30 groups and within the 90-50 groups.

It was expected that the preparative variables studied might have different degrees of importance for different oils and surfactants. The chemical and physical nature of the nonaqueous liquids and the emulsifiers used in this investigation constitute additional, nonstatistical variation. The

experimental design was applied to each combination of the following four nonaqueous liquids and thirteen surface-active agents.

Oils	Surfactants
Paraffinic mineral oil (Marcol GX)	Cetylethylmorpholinium ethosulfate (G-263)
Cottonseed oil (Wesson oil)	Isopropylammoniumdodecylbenzenesulfonate (IPADBS)
Oleic acid (Emery 233LL)	Polyoxyethylene (100) stearate (G-2159)
Methylphenyl silicone (Dow Corning 710 Fluid)	Polyoxyethylene (8) stearate (Myrj 45)
	Polyoxyethylene (23) lauryl alcohol (Brij 35)
	Polyoxyethylene (15) nonyl phenol (Renex 678)
	Polyoxyethylene (20) sorbitan monostearate (Tween 60)
	Polyoxyethylene (20) sorbitan monooleate (Tween 80)
	Polyoxyethylene (5) sorbitan monooleate (Tween 81)
	Sorbitan monolaurate (Span 20)
	Sorbitan monostearate (Span 60)
	Sorbitan monooleate (Span 80)
	Sorbitan trioleate (Span 85)

A trademark or other designation is stated in parentheses following the name of each oil and surfactant.

Thus, with 12 methods for each emulsifier-substrate combination, 624 emulsion preparations were made. Their emulsion type and stability are the data reported in this study. It must be emphasized that the object of this investigation was not to determine the optimum methods for emulsifying each oil under consideration but, rather, to determine the importance of the preparative variables studied in influencing emulsion type and stability.

EXPERIMENTAL

In addition to the variables specified in the elements of the experimental design, the following general procedure was followed in the preparation of the emulsions. Distilled water and oils were measured by volume and emulsifier by weight. Relatively less vigorous agitation was obtained with a propeller, while more vigorous agitation was obtained with an Eppenbach Homo-Mixer which is an enclosed turbine type of stirrer. Glass apparatus was used throughout, except for the propeller shaft and blade and the Homo-Mixer. All of one phase was added to the other at one time, with agitation. Agitation, whether by propeller or by means of the Homo-Mixer, was continued for five minutes after addition was completed. In making emulsions at 70°C., both the water and the oil were previously brought to this temperature. Emulsion type was determined by the dilution technique. Emulsion stability was observed in an Atlab viewer (6). Stability was evaluated initially approximately ten minutes after emulsion preparation, after one day and after one week.

RESULTS

The stability of the emulsions formed was expressed on a numerical scale of 9 to 0, excellent stability being represented by 9. This qualitative

scale includes the more commonly observed gradations of emulsion separation, as given in the following descriptions of the stabilities corresponding to each rating.

Emulsion Description	Numerical Rating
No visible separation	9
Emulsion is nearly homogeneous without definite separation	8
Emulsion shows faint cream line	6
Creaming with separation of 1% or less oil or water	5
Emulsion has creamed with separation of significant volumes of oil and aqueous phases	4
Almost complete separation of emulsion	2
Complete separation into components with essentially their original volume	1

Typical results for each of the twelve preparative methods for one oil-emulsifier pair are illustrated by those for paraffinic mineral oil and Tween 60 emulsifier in Table 2. In some cases, as in method 10 in this set, it was not possible to measure the emulsion type because of the poor stability of the resulting emulsion.

TABLE 2—EMULSION TYPE AND STABILITY—MINERAL OIL-TWEEN 60 EMULSIFIER

Method No.	Water, %	External Phase	Stability		
			Initial	24 Hr.	1 Wk.
1	90	w	4	4	4
2	90	w	4	4	4
11	90	w	5	4	4
12	90	w	4	4	4
5	50	w	4	4	4
8	50	w	4	4	4
9	50	w	5	4	4
10	50	..	2	2	1
3	30	o	2	2	1
4	30	o	2	2	2
6	30	o	2	2	1
7	30	w	9	5	4

Emulsion Type

The results of the statistically designed experiment may be analyzed for both emulsion type and for stability. Some emulsifier-oil combinations, indicated in Table 3, produced predominantly o/w emulsions. Such combinations, leading mainly to o/w emulsions, may be divided into three groups: (1) those forming only o/w emulsions with all 12 methods, designated in Table 3 by o/w; those forming o/w emulsions or emulsions of nonmeasurable type, designated in Table 3 by X; and those forming one w/o emulsion together with o/w emulsions and nonmeasurable types, designated in Table 3 by the method number forming a w/o emulsion.

TABLE 3—PREDOMINANTLY O/W EMULSIONS

Emulsifier	Mineral Oil	Cottonseed Oil	Oleic Acid	Methyl-phenyl Silicone
G-263		#3		o/w
IPADBS		o/w		o/w
G-2159				X
Brij 35		#3		o/w
Tween 60		#6		o/w
Tween 80		#6	#6	o/w
Renex 678		X		o/w
Myrj 45	#6	#6		#6
Tween 81		#6		o/w
Span 20				
Span 60		#4		
Span 80				
Span 85				

o/w = all o/w emulsions; X = o/w or nonmeasurable; numbers are the preparative methods forming one w/o emulsion per set of 12 procedures in the experimental design (Table 1).

In these cases, the character of the emulsifier and oil in combination determine that the oil is to be the discontinuous phase of the emulsion. For the emulsifier-oil pairs indicated in Table 3, within the limits of these experiments, it is evident that the preparative variables have little or no influence on the emulsion type formed. Where blanks occur in Table 3, two or more w/o emulsions were formed for each emulsifier-oil combination. The combinations indicated by blanks are capable, at least to some extent, of being made to form either o/w or w/o emulsions by the influence of one or more preparative variables. It is with these combinations that the results of the experimental design have yielded information on the importance or lack thereof of the six preparative variables on emulsion type formed.

To evaluate the importance of the different preparation factors, an arbitrary scale was applied to the emulsion type results: an o/w emulsion was assigned a value of +1, a w/o emulsion, a value of -1 and a nonmeasurable type a value of zero. (Stability of emulsions was not considered in connection with the emulsion type evaluations.) The indicated numerical values were algebraically summed for each factor for the four experiments with 90 per cent of water and for the four experiments with 30 per cent of water, the difference between these two groups determined and divided by four to obtain average values. The magnitude of this difference is a measure of the relative importance of each level of the factor studied. The calculation is illustrated by the results for each factor for mineral oil emulsified with Tween 60.

In this case, the quantity of water is seen to be more important than the other factors. There were 30 emulsifier-oil combinations forming two or more w/o emulsions when the 90-30 groups of experiments were compared; similarly, nine combinations fitting this criterion were found with the

90-50 groups. The distributions of average differences are shown in Tables 4 and 5 for each factor.

Inspection of the frequency of differences reveals the overwhelming importance of quantity of water compared to the other factors. This is evident in both the 90-30 and the 90-50 comparisons. In the cases of surfactant concentration, surfactant location, temperature and methods of agitation the values of the differences are small (0 to 1.00) in relation to the differences found in the case of proportion of water (1.00 to 2.00). It is concluded that these preparative variables are of little importance in determining emulsion type. In the case of addition order, a partial concentration of differences at a value of 1.00 is suggestive that this factor has some importance in determining emulsion type. The conclusion that larger quantities of water and adding oil to water leads to o/w emulsions while the reverse leads to w/o emulsions is consistent with emulsion technology practices.

A confirmation of this conclusion is obtained by noting the common factors in the methods which yielded only one w/o emulsion from the set of experiments with several emulsifier-oil combinations (Table 3). To form an emulsion of the opposite type from that which is predominately determined by the nature of the emulsifier and oil indicates considerable importance for one or more factors in the singular preparation methods. Method 6 appears in this category seven times, method 3 appears twice and method 4 once. The only common factor in these three methods (Table 1) favoring w/o emulsions is the use of 30 per cent water. No other factors are common to all three of these preparation methods. In methods 6 and 4, water is added to oil.

Emulsion Stability

In the analysis of the stability results, a procedure similar to that employed to evaluate the influence of the six preparative variables on emulsion type was used. Thus the stability values for a given emulsifier-oil pair for the 90, 50 and 30 per cent experiments were summed, and averaged differences were calculated for the 90-30 and 90-50 groups. Combination of stability results for

o/w w/o Sum Diff. Divide by 4	Emulsifier Conc., %		Water, %		Emulsifier Location		Temp., °C.		Order of Addition		Agitation	
	1 ex.	2.5	90 ex.	30	0 ex.	w	25 ex.	70	0 → w ex.	w → 0	0 ex.	H
+2												
-2												
0												
+3												
-1												
+2												
0												
+4												
+4												
+1												
-3												
-2												
0												
+2												
-2												
0												
+3												
-1												
+2												
0												
+2												
-2												
0												
+2												
-2												
0												
+3												
-1												
+2												

TABLE 4—EMULSION TYPE 90-30 (30 CASES)
Frequency of Differences

Average Difference between Levels (effects)	Emulsifier Conc.	H ₂ O, %	Emulsifier Location	Temp., °C.	Order of Addition	Agitation
0	7		8	3	5	5
0.25	5		6	7	6	4
0.50	13		10	11	7	13
0.75	5		5	4	5	7
1.00		7	1	5	7	1
1.25		8				
1.50		12				
1.75		2				
2.00		1				

TABLE 5—EMULSION TYPE 90-50 (9 CASES)
Frequency of Differences

Average Difference between Levels (effects)	Emulsifier Conc.	H ₂ O, %	Emulsifier Location	Temp., °C.	Order of Addition	Agitation
0	3		3	1	1	4
0.25	1		1	1		2
0.50	4		4	4	2	2
0.75	1		1	1	1	
1.00		5		2	5	1
1.25		2				
1.50		2				

both o/w and w/o emulsions, however, would be inappropriate. To circumvent this difficulty, the following procedure was used. In the analysis of the factors leading to stable o/w emulsions, the stabilities of the w/o emulsions were designated as zero, regardless of their observed value. Nonmeasurable emulsion types were treated in the same way. In the analysis of w/o emulsions, a value of zero similarly was assigned to the stability of the o/w emulsions formed with the same emulsifier-oil pair.

Computations of the differences between the values of the two levels for each of the six factors investigated were carried out by means of an IBM 650 computer. As an example of the differences found between the two levels, the results pertaining to stability of o/w emulsions after one day, for the factor of emulsion concentration, are shown in Table 6. The sign of the difference values indicates which level of the factor under study may have significance. Thus a positive value means that a 2.5 per cent level of emulsifier favors the formation of a stable o/w emulsion, whereas a negative value indicates that 1 per cent emulsifier favors a stable o/w emulsion.

TABLE 6—EMULSIFIER CONCENTRATION—ONE DAY STABILITY OF O/W EMULSIONS
Average Value of Stability Differences of 1% and 2.5% Emulsifier (90-30 groups)

Emulsifier	Mineral Oil	Cottonseed Oil	Oleic Acid	Methyl Phenyl Silicone
G-263	1.25	1.25	2.25	-0.50
IPADBS	2.25	2.00	1.25	1.25
G-2159	2.25	2.25	1.25	0
Brij 35	2.25	1.00	0.50	0.25
Tween 60	1.25	2.25	1.75	-0.25
Tween 80	1.25	2.25	2.00	-0.25
Renex 678	0.25	1.00	2.25	-0.25
Myrj 45	4.00	3.00	-0.50	2.75
Tween 81	0.75	2.50	-0.75	0
Span 20	1.25	1.50	2.50	0.75
Span 60	4.25	2.00	2.25	2.25
Span 80	2.00	1.25	2.25	1.25
Span 85	1.00	1.00	-0.50	1.00

+ means 2.5% is favored for a stable o/w emulsion.

- means 1% is favored for a stable o/w emulsion.

In order to determine the magnitude of difference values which are significant, the frequency of these differences were tabulated. Results of the differences between levels for all factors for initial stability are recorded in Fig. 1. Inspection of this plot indicates a distribution of small difference values about zero. These observed deviations evidently represent normal experimental variation and are considered to be without significance. A high concentration appears at difference values of 2.00-2.25, followed by lower frequencies for still higher differences. Similar results were obtained in the plot of stability differences at one day and one week.

An alternative approach to the limit of difference which is significant involves the following considerations. It is believed that one unit on the stability scale is the maximum error which is to be expected. To evaluate one variable for an emulsifier-oil pair, the four stability results for one level are subtracted from the four stability results at the alternative level, and the difference is averaged by dividing by four. Should all four stability results at one level deviate by one in the same direction and all four results at the other level deviate by one in the opposite direction, the averaged difference would be given by:

$$\frac{(+1+1+1+1) - (-1-1-1-1)}{4} = 2.00$$

Thus the largest variation that would be expected from variations in stability observation is 2.00. Significant deviations from zero are conservatively estimated, therefore, to begin at a difference of 2.00, both on the basis of the observed distributions of differences and the maximum expected errors in stability ratings.

On the basis of this criterion, less than half of the systems evaluated

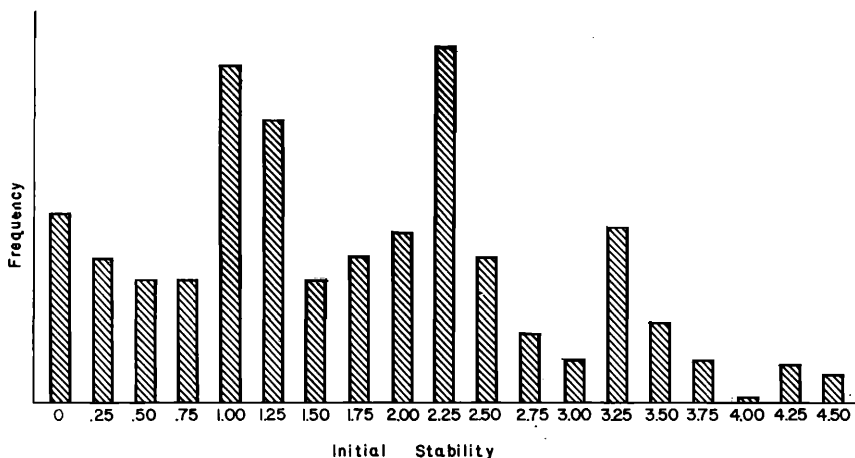


Figure 1—Differences between levels - all factors

showed significant dependence on the preparative variables. As an example, the significant differences found for the factor of temperature are indicated in Table 7. Similar organization of the data was made for each preparative factor. In addition to the criterion of a difference between levels of 2.00 or greater, the practical criterion of an indication of stability beyond that measured initially was imposed. For a given emulsifier-oil pair, it was decided that a factor was significant only if significant difference values appeared for at least the initial and one-day stability or for the one-day and one-week stability observations. If a significant difference appeared at only one time period but not at the other two, the factor in question was not considered to be important in contributing to the stability of the emulsion obtained from the oil-emulsifier pair in question.

Stability of the o/w emulsions formed was greater than that of the w/o emulsions. As had been expected, it was found that the nature of the oil and the nature of the surfactant are of prime importance in determining the stability of the resulting emulsions. Indeed, of the 312 emulsifier-oil-variable comparisons of the 90-30 groups which were made for o/w emulsions, 226 showed no significant dependence of stability on any individual preparative factor by the criteria used in this analysis. Thus the results of this study have reaffirmed the view that the procedure used is often of secondary importance in emulsion stability. The relation of chemical constitution and physical characteristics of oil and emulsifier to stability and other emulsion characteristics is under active investigation in this laboratory (2, 3, 7). The 13 emulsifiers used in this investigation represent a variety of chemical types and hydrophile-lipophile balances. Similarly, the four oils investigated are of different chemical types.

TABLE 7—TEMPERATURE-SIGNIFICANT DIFFERENCES O/W EMULSIONS (90.30)

Emulsifier	Mineral Oil			Cottonseed Oil			Oleic Acid			Methylphenyl Silicone		
	Init.	One Day	One Week	Init.	One Day	One Week	Init.	One Day	One Week	Init.	One Day	One Week
G-263	-2.25						-2.50	-2.25				
IPADBS	-2.25	-2.25					-3.50	-3.25	-2.25			
G-2159	-3.25	-2.25	-2.25	-3.25	-2.25	-2.25	-5.50	-3.25	-2.25			
Brij 35	-2.25	-2.25		+2.25								
Tween 60	-2.50			-3.25	-2.25	-2.00	-2.25					
Tween 80	-2.25			-3.25	-2.25	-2.00	-2.25					
Renex 678	-4.50	-2.25	-2.00	-3.25	-2.25	-2.00	+3.50	+2.25				
Myrij 45	-4.25	-4.00	-3.00	-4.25	-2.50	-2.75				-2.00		
Tween 81												
Span 20												
Span 60	-4.50	-4.25	-3.25	-7.0	-7.0	-5.5				-4.25	-4.25	-4.25
Span 80	-2.50	-2.50	-2.00	-2.25			-3.25	-2.25	-2.00	-3.25	-3.25	-2.50

+ means 25° is favored for a stable o/w emulsion.

- means 70° is favored for a stable o/w emulsion.

The extent to which preparative variables are important for stability of the emulsion made from the emulsifiers and oils studied is indicated in Table 8 for o/w emulsions and in Table 9 for w/o emulsions. In these tables is listed, for each preparative variable, the level of the experimental design showing significance; in addition, the number of emulsifier-oil pairs for each oil exhibiting significance at this level is shown. In the case of o/w emulsions, it is evident that higher emulsifier concentration (2.5 per cent), higher concentration of water (90 per cent) and higher temperature (70°C.) appear to be of importance in conferring stability on mineral oil, cottonseed oil and oleic acid o/w emulsions. Addition of oil to water, under the conditions used, was less frequently of importance to the formation of stable o/w emulsions. Although placing the surfactant in water as opposed to oil is favored in the case of mineral oil, this factor is less important or nonexistent for the other nonaqueous liquids. Agitation by means of the Homo-Mixer instead of by propeller appears to be of value with mineral oil. The number of significant factors is appreciably less with methylphenyl silicone than with the other three oils. It may be concluded for the range of emulsifiers tested that the chemical or physical nature of this oil primarily determines the stability of its emulsions.

Few preparative factors were found to be important for the stability of w/o emulsions. Of the 42 emulsifier-oil pairs which formed at least one w/o emulsion, there are 252 emulsifier-oil-variable comparisons possible; only 20 were found to be significant. A small proportion of water

TABLE 8—FREQUENCY OF VARIABLE LEVELS SIGNIFICANTLY FAVORING STABILITY OF O/W EMULSIONS (90-30)

Oil	Emulsifier Conc., %	Water, %	Emulsifier Location	Temp., °C.	Order of Addition	Agitation
Mineral Oil	2.5 (6)	90 (6)	w (4) o (1)	70 (7)	o → w (4)	H (5) P (1)
Cottonseed Oil	2.5 (6)	90 (3) 30 (1)	o (1)	70 (5)	o → w (2)	H (1)
Oleic Acid	2.5 (6)	90 (4)	w (1) o (2)	70 (4) 25 (1)	o → w (3)	H (2)
Methylphenyl Silicone	2.5 (2)	90 (1) 30 (1)	w (1) o (1)	70 (2)	o → w (1)	H (1)

Frequencies of significant levels are shown in parentheses.

TABLE 9—FREQUENCY OF VARIABLE LEVELS SIGNIFICANTLY FAVORING STABILITY OF W/O EMULSIONS (90-30)

Oil	Emulsifier Conc.	Water, %	Emulsifier Location	Temp., °C.	Order of Addition	Agitation
Mineral Oil		30 (4)				
Cottonseed Oil		30 (1)				
Oleic Acid		30 (6)		25 (2)	w → o (2)	
Methylphenyl Silicone		30 (3)		25 (1)	w → o (1)	

Frequencies of significant levels are shown in parentheses.

(30 per cent) appears as a significant factor at least once for each oil. With oleic acid and methylphenyl silicone, a low preparation temperature (25°C.) and addition of water to oil were found to be significant in a few cases. Thus, with w/o emulsions as compared to o/w the chemical and physical nature of the oil and emulsifier is even more important than preparative variables in determining stability.

In summary, within the limits studied, the results of the statistically designed experiment applied to four oils and thirteen surfactants have confirmed the previously known importance of a high proportion of water in making stable o/w emulsions and a small proportion of water in making w/o emulsions. Of discernible, but lesser, significance to emulsion type and stability is the addition order; adding oil to water yields the expected o/w emulsion. Higher levels of emulsifier concentration and a higher preparative temperature are important in conferring stability on o/w emulsions. Emulsifier location and, within the experimental limits studied, method of agitation do not exhibit consistent significance. In a large number of the emulsifier-oil pairs studied, particularly those forming w/o emulsions, none of the individual preparative variables showed significance in determining stability. It is evident that the chemical and physical nature of particular emulsifiers and oils in combination have a major influence on the type and stability of emulsions which are formed.

Acknowledgment: The authors wish to express their appreciation to B. N. Baer, A. N. Green, A. M. Levine, R. D. Charles and P. Becher for their several contributions to this study.

(Received May 8, 1962)

REFERENCES

- (1) Becher, P., "Emulsions: Theory and Practice," ACS Monograph No. 135, New York, Reinhold Publishing Corp. (1957), pp. 209-244.
- (2) Becher, P., *J. Soc. Cosmetic Chemists*, **9**, 141 (1958).
- (3) Becher, P., *Ibid.*, **11**, 325 (1960).
- (4) Davies, O. L., "Design and Analysis of Industrial Experiments," London, Oliver and Boyd (1954), pp. 484-485.
- (5) Griffin, W. C., in "Encyclopedia of Chemical Technology," Vol. 5, New York, The Interscience Encyclopedia, Inc. (1950), pp. 692-718.
- (6) Griffin, W. C., and Behrens, R. W., *Anal. Chem.*, **24**, 1076 (1952).
- (7) Ross, S., Chen, E. S., Becher, P., and Ranauto, H. J., *J. Phys. Chem.*, **63**, 1681 (1959).