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# A study in emulsions

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## A STUDY IN EMULSIONS

Edward A. Morse

Sponsored by: Johnson & Johnson Research Division

Newark College of Engineering Staff Consultant - Dr. Charles Mantell

Johnson & Johnson Research Consultants: J. N. Masci and E. G. Hart

### A STUDY IN EMULSIONS

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Library Newark College of Engineering

#### PART I: INTRODUCTION

An emulsion is a dispersion of one liquid in another liquid, the liquids being insoluble in each other. An emulsion consists of two phases, a continous phase and a dispersed phase. The dispersed phase consists of tiny droplets or particles of one liquid which is completely surrounded by the other liquid conprising the continous phase. One of the many factors affecting the stability of an emulsion is the size of the particle of the dispersed liquid.

This study is concerned with one emulsion prepared by different mechanical devices and under different conditions. The units of equipment employed are Eppenbach Colloid Mill, Marco Homogenizer, Lightnin' Mixer and Master Counter-current Mixer. Samples of the emulsion prepared by these methods will be retained for particle size determinations. All samples will be stored in a constant temperature room at 70° F.

The ultimate aim of this study is to indicate the effectiveness of each of the emulsifying units studied. It is also desired to show how the particle size of the dispersed phase changes on aging. The stability of all samples was closely followed to discover any trends of instability.

A search of the literature reveals only fragments of information concerning particle size analysis with regard to commercial preparation of emulsions. In the previous work on emulsions, standard laboratory methods of dispersion were usually used. It is hoped that this study combined with past and future studies will point to some definite mechanical system to produce the optimum commercial emulsion.

#### PART II: THE EMULSION

The emulsion used in this study is mineral oil dispersed It was deemed advisable to use an emulsion with poor stability so that differences in stability could be noted quickly. For the emulsifying agent a common soap type was considered to be the best for a basis of comparison with other work done in the emulsion field. The final choice was triethanolamine stearate formed in the emulsion by reacting triethanolamine in the water phase, with stearic acid in the oil phase. In order to formulate an emulsion with poor stability, the usual stabilizers or gums were omitted from the emulsion formula; thus the emulsion will be comprised of four ingredients; mineral oil, water, triethanolamine and stearic acid. It remains then to decide on the percentages of these ingredients. Considering first the mineral oil, many authors advise that for an oil in water type emulsion, the oil percentage should be below 45%, so to be well below the recommended percentage, it was decided to use 30% mineral oil.

The percentage of triethanolamine which determines the percentage of emulsifying agent presented a problem. A test emulsion was made using 1% triethanolamine and 4% stearic acid. This emulsion was made in the Eppenbach Colloid Mill. Settings of 60, 30, 10, 5 and 2 on the micrometer were used. On aging, this emulsion showed no tendency to separate after three weeks.

Part II: The Emulsion, Cont'd:

This was a little too stable for the purposes of this study. It was therefore decided to use \$\mathbb{H}\$ of triethanol-amine and 2% of stearic acid. The stearic acid percentage being in excess of the required amount to form \$\mathbb{H}\$ triethanol-amine stearate. The water percentage obtained by difference being 67.5%. Distilled water was used to avoid the complications of hardness factors. The emulsion formula then is as follows:

Mineral Oil	30.0 %
Water (Distilled)	67.5 %
Triethanolamine	.5 %
Stearic Acid	2.0 %
	100.0 %

#### PART III: PARTICLE SIZE DETERMINATION

The size-frequency analysis of the emulsions was accomplished by direct microscopic observation. A Bausch and Lombe microscope was used with a 25 ocular and 20% lens. The right ocular was scaled. Under these conditions, 0.2 of a scale segment equals 1 micron. Hemacytometer slides of .1 mm. depth were employed for the observations.

Samples of the emulsion were taken while it was agitated to insure the uniformity of the mass and sample. One drop of the sample was placed in approximately 300 cc. of 0.5% methocal solution. The dilute sample was then thoroughly mixed. The slide was prepared by placing one drop of the dilute solution on the raised portion of the hemacytometer and then covering with a cover glass. The purpose of the dilute methocal sample is two-fold.

First, the dilution is necessary to obtain a slide with the oil particles distinctly separated. Secondly, the viscosity of the methocal solution stops the Brownian movement of the oil droplets. The measuring of the droplets is accomplished by bringing them into sharp focus and rotating the scaled ocular into position.

The counts were made using the size ranges as follows: under 1 micron, 1 - 2 microns, 2 - 4 microns, 4 - 8 microns and 8 - 16 microns. The size-frequency analysis obtained by this method is best presented in the form of a histogram with the X axis units of size and the Y axis percentage of total particles counted.

In some cases, the average particle size was desired. This was calculated by multiplying the arithmetic mean diameter of each size group by the percentage of particles in the group totaling all the figures thus obtained together and then dividing by 100.

#### PART IV: EPPENBACH COLLOID MILL

The Eppenbach Colloid Mill is a mechanism for reducing the size of particles of emulsions or suspensions. The emulsion is whirled violently by a rotor through a small gap between the rotor and a stator. The rotor and stator have teeth on the initial section but are smooth on the final surface. The gap between the rotor and stator may be adjusted by a micrometer screw setting. The rotor speed is constant at 7000 revolutions per minute.

The emulsion was prepared by heating the mineral oil and stearic acid until a clear solution was formed. The temperature was 120° F. . The water and triethanolamine were mixed together and the oil phase was added slowly to the water phase while stirring with a large spatula. In order to fully investigate the entire range of the micrometer adjustment of the mill, three batches of emulsion were prepared. A total of 14 micrometer settings were used. An eight ounce sample was taken at each setting and retained for study.

The plot of average particle size versus micrometer setting (space between rotor and stator) appears to be a step function at first glance; however, a close examination of the data and the slides of the emulsions indicate that the steps are due to the grouping of particles into size groups instead of taking individual sizes of each particle.

The first step on the graph comes between micrometer setting 20 and 30. A close examination of the particles in the emulsion made at the 20 setting shows a great number of particles just under a micron in size. In the emulsion made at the 30 setting, the size of the majority of particles has shifted to just over a micron in size and are now in the 1 - 2 micron group. When calculating the average particle size of each emulsion, the large group of particles in the emulsion made at the 20 setting would be calculated as being .5 microns while the large group of particles in the emulsion made at the 30 setting would be calculated as being 1.5 microns. Actually the particles are just a little under and a little over a micron - a spread of about .2 microns and not 1.0 microns as occurs in the average sizes. It was decided therefore to draw an average curve through the mid-points of the steps. This curve should represent the actual average particle size of the emulsions.

Part IV: Eppenbach Colloid Mill. Cont'd:

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Cooper studied 60 emulsions passed through a Hurrell Colloid Mill in which he varied the size of the gap and the speed of the rotor. His report indicated that with this mill there was no change in the average particle size of the emulsion. His method of size-frequency analysis was a photographic type which he says may have been somewhat inaccurate, especially so far as smaller particles were concerned.

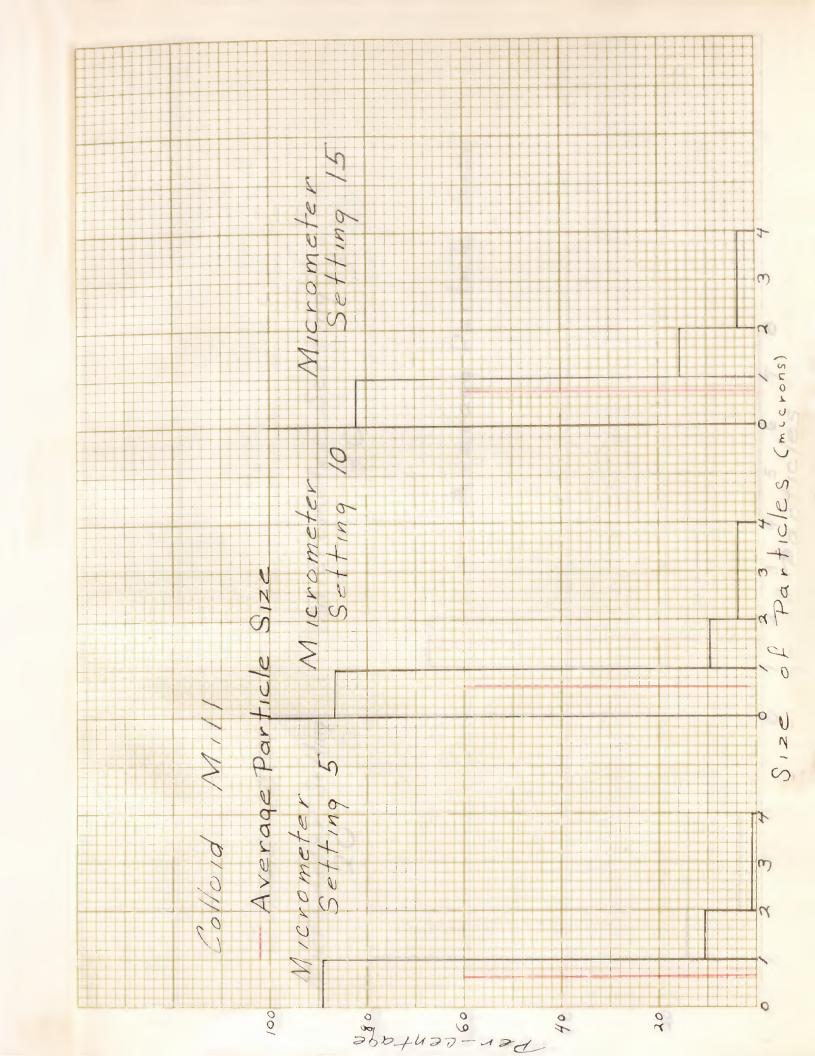
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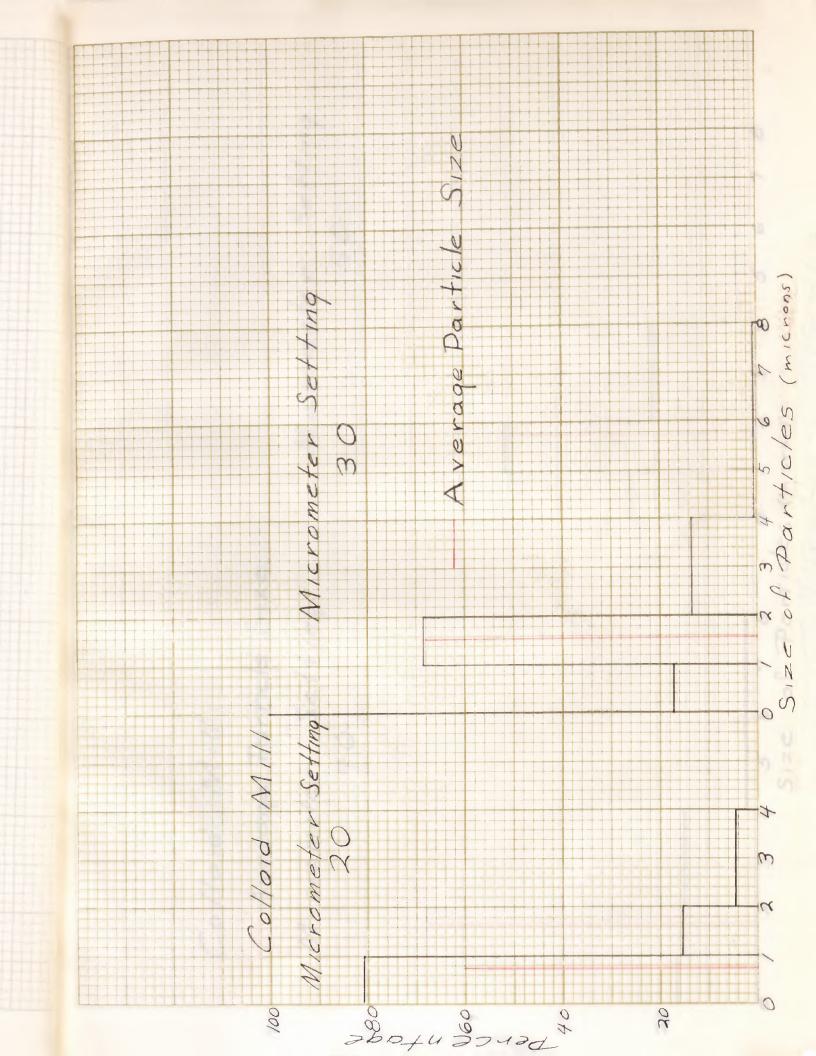
Sibree reported a size-frequency analysis of an emulsion passed through a Hurrell Colloid Mill, but did not report the condition of operation or any variation in particle size with operating conditions.

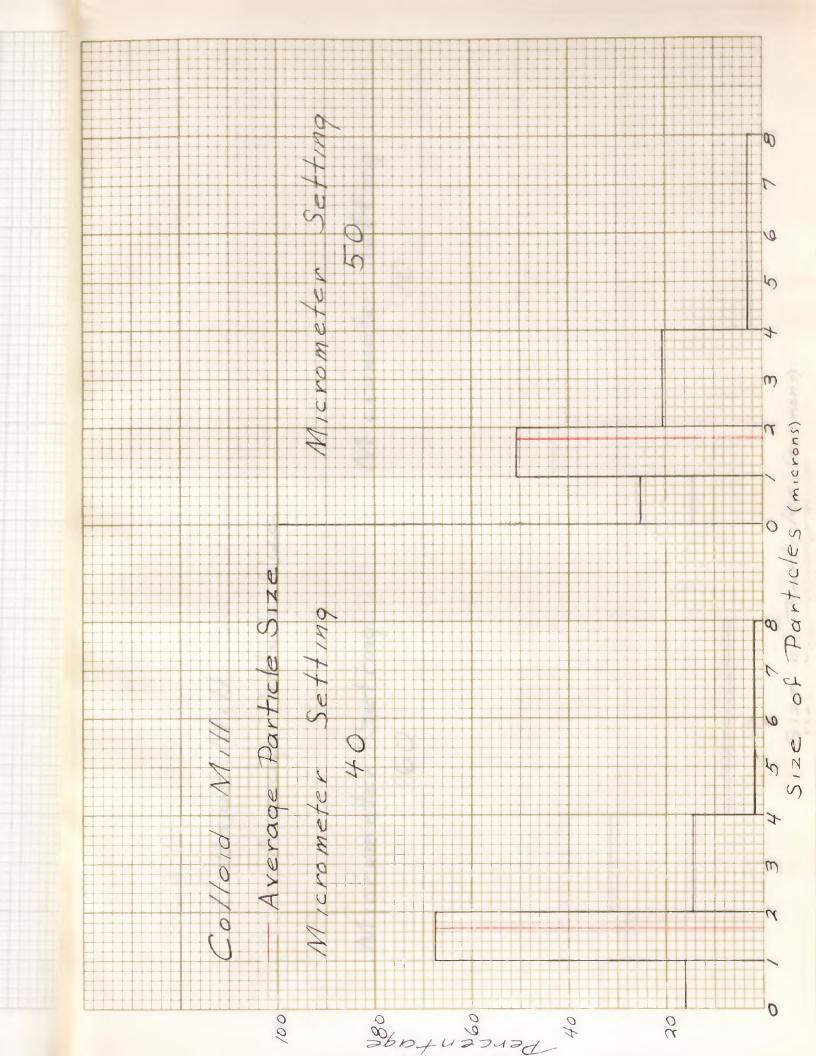
3

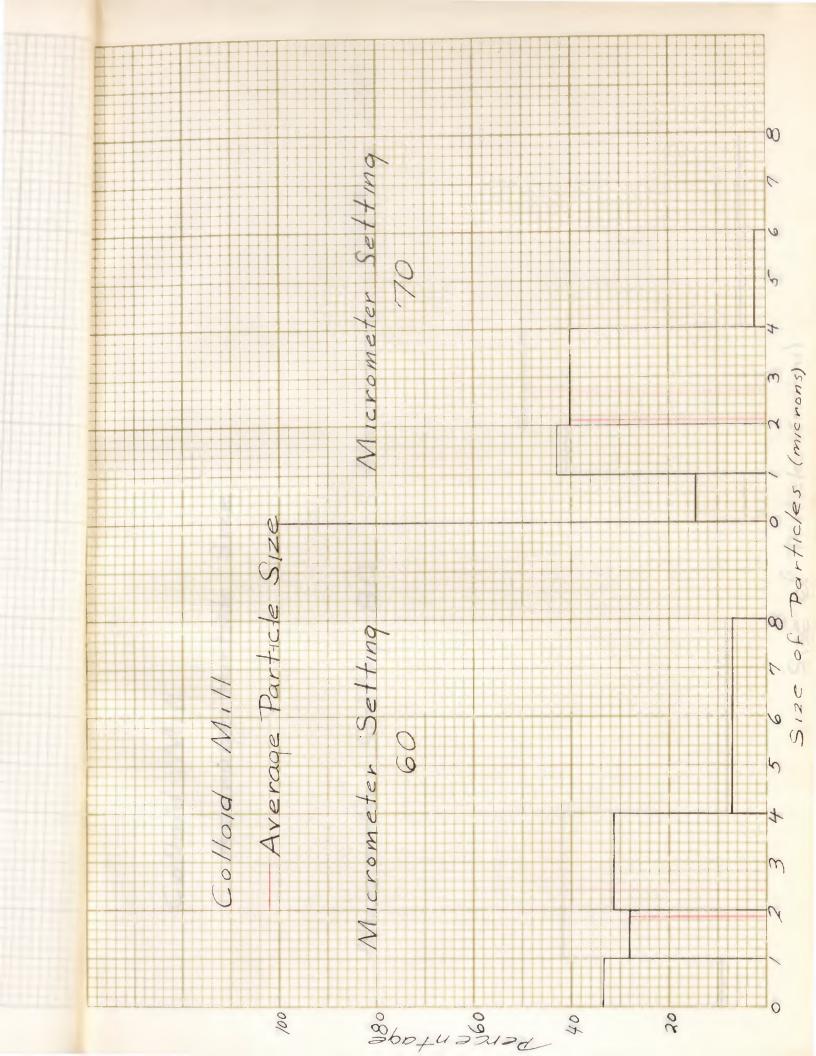
Gabriel shows comparative photographs of an alsohaltic bitumen emulsion prepared by a colloid mill and a slow speed mixer.

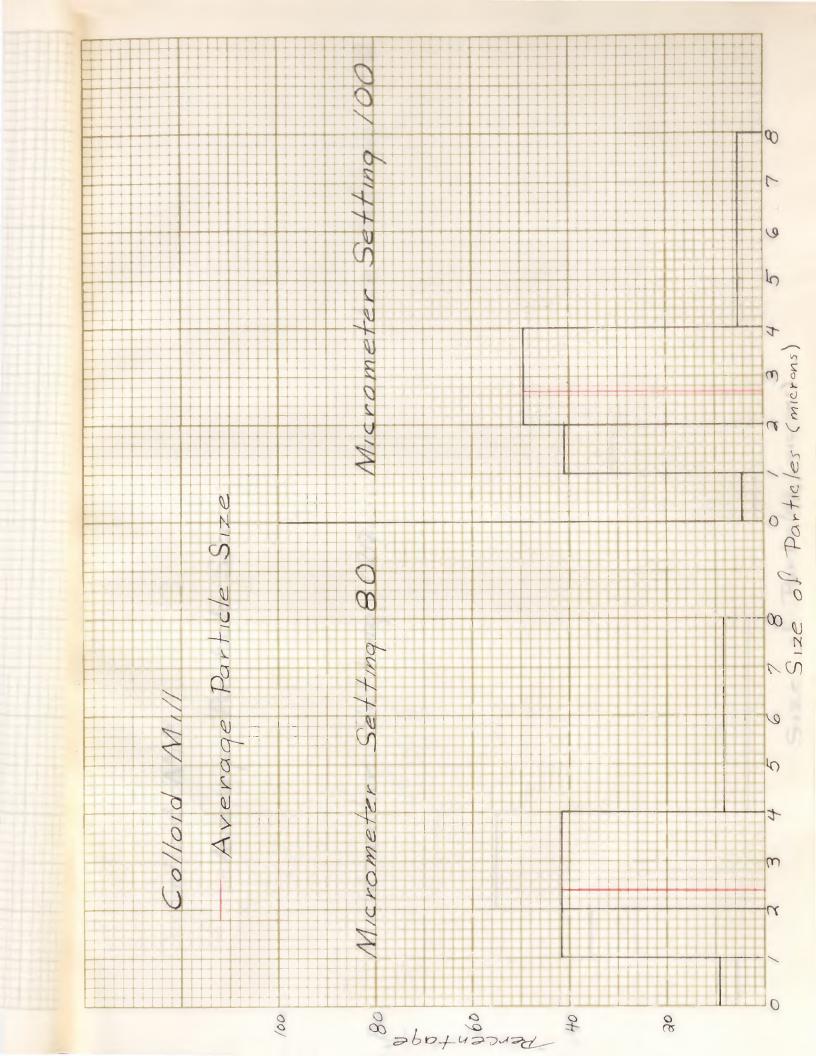
- (1) Cooper J. Soc. Chem. Ind. 56, 447 T 1937
- (2) Sibree Trans. Faraday Soc., 27, 173, 1931
- (3) Gabriel Technical Aspects of Emulsions London: Harvey

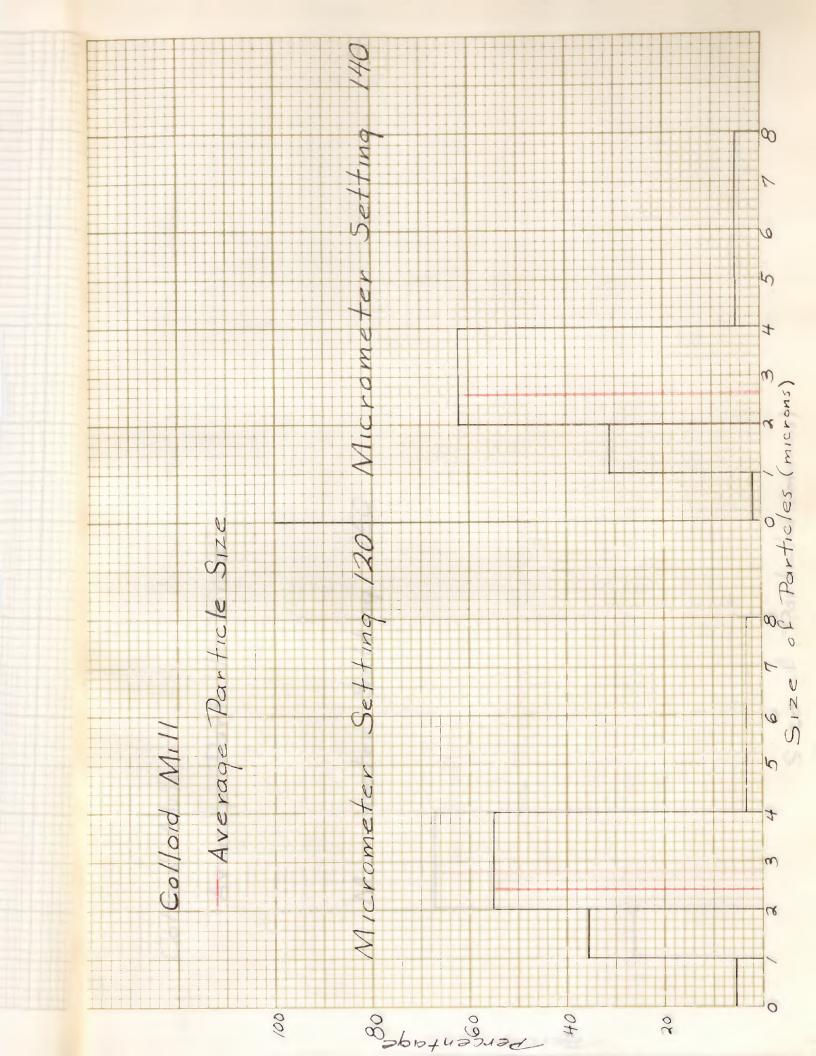


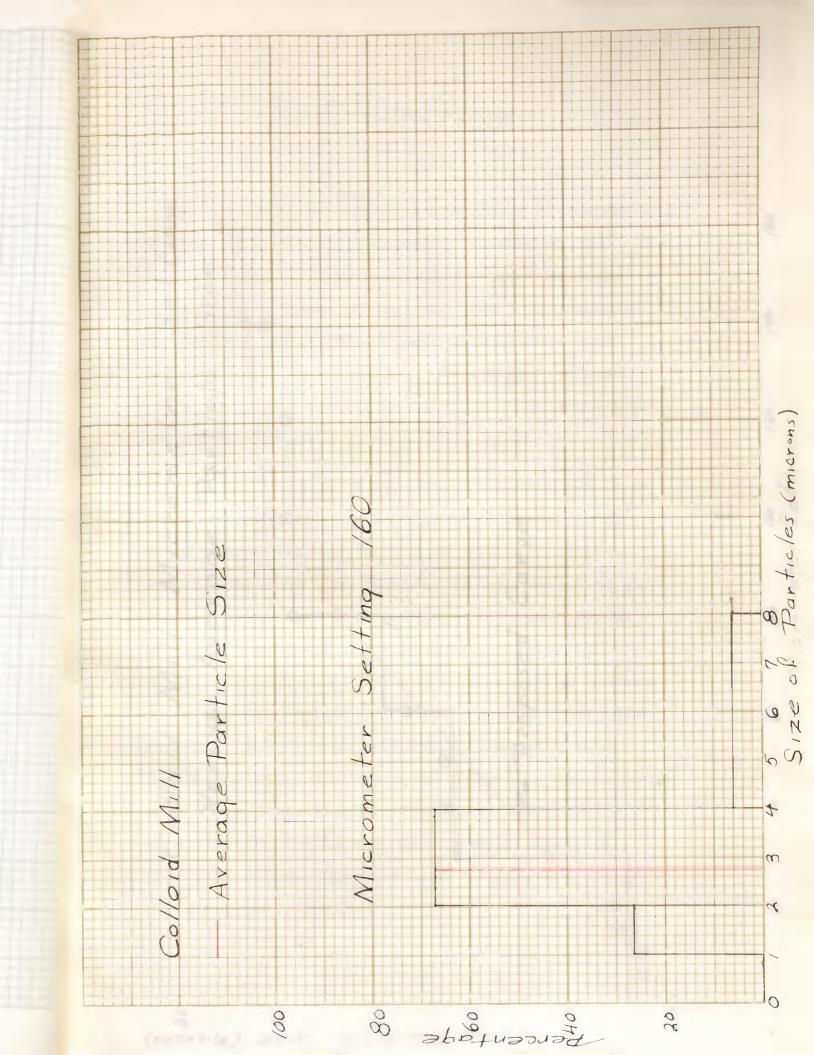


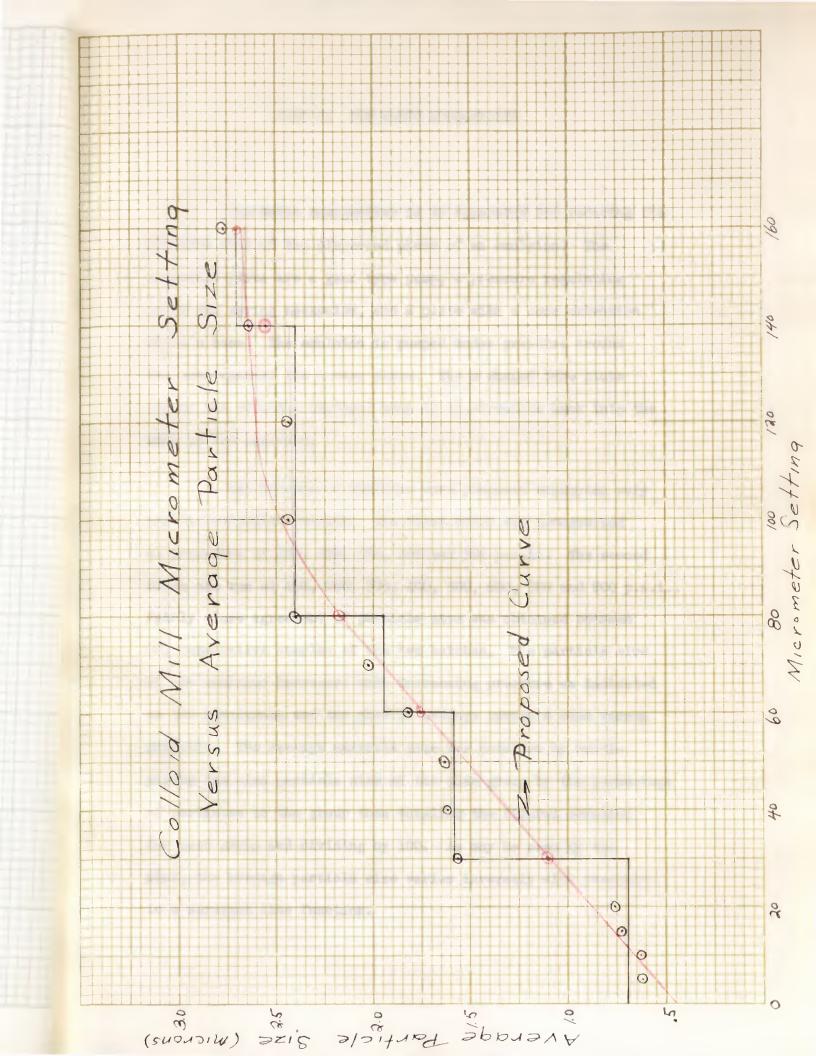












## PART V: THE MARCO HOMOGENIZER

The Marco Homogenizer is an apparatus for reducing the particle size of the dispersed phase of an emulsion. The essential parts are a gear type pump, a pressure regulating screw and spring mechanism, and a plate with a cone extension and a u base. The emulsion is pumped under pressure around the cone against the u base plate. The u shaped base plate forces the emulsion impinged upon it to circulate back into the mass of the emulsion.

Two batches of emulsion were prepared employing very little preliminary mixing. The first batch was homogenized at pressures of 100, 200, 300, 400 and 500 p.s.i.. The second batch was run at 100, 200, 300, 400, 500, 600, 700 and 800 p.s.i.. Fairly close agreement of particle size was obtained between the comparative samples of the two batches. The particle size of the emulsion decreased with increasing pressure as indicated on the histograms and the plot of average particle size versus pressure. The average particle size was obtained by multiplying the mean particle size of the size group by the percentage of particles in the group then totaling the figures obtained for each group and dividing by 100. As may be seen by the plot, the average particle size varies inversely with pressure in a straight line function.

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Sibree reports size-frequency analysis of a viscous paraffin emulsion made in a "Viscoliser" homogenizer at a pressure of 2000 lbs. per square inch. No attempt was made to determine particle size variation with pressure in his work. He did show, however, that the size-frequency analysis varied for different emulsions produced under the same conditions.

2

Dorey made size frequency analysis of 16 emulsions.

He prepared the emulsions in four ways as follows:

- a. 10 minutes stirring with a Beach Mixer.
- b. 5 minutes stirring with a Beach Mixer anda pass through an Impulsor Emulsifier
- c. phases fed separately into the Impulsor Emulsifier,
- d. part of the emulsion in part C was put through the homogenizer for a second time.

His work indicated that 10 minutes stirring was not as effective in reducing particle size as 5 minutes stirring and homogenization. It was also discovered that two homogenizations were better than one. This seems to indicate that the final particle size of an emulsion passed through a pressure type homogenizer depends upon the particle size of the feed emulsion. His report proved that smaller particles were obtained with a soap type emulsifier when the soap constituents were added separately with the water and oil phases as was done with the emulsion employed in this study.

Part V: The Marco Homogenizer, Cont'd:

3

Hatschek reported an increasing number of small particles with repeated homogenization.

4

Smith and Grinling experimented with a cod liver oil emulsion and published data showing that an emulsion stabilized by gum has a larger arithmetical mean diameter of dispersed particles than an emulsion without gum after homogenization.

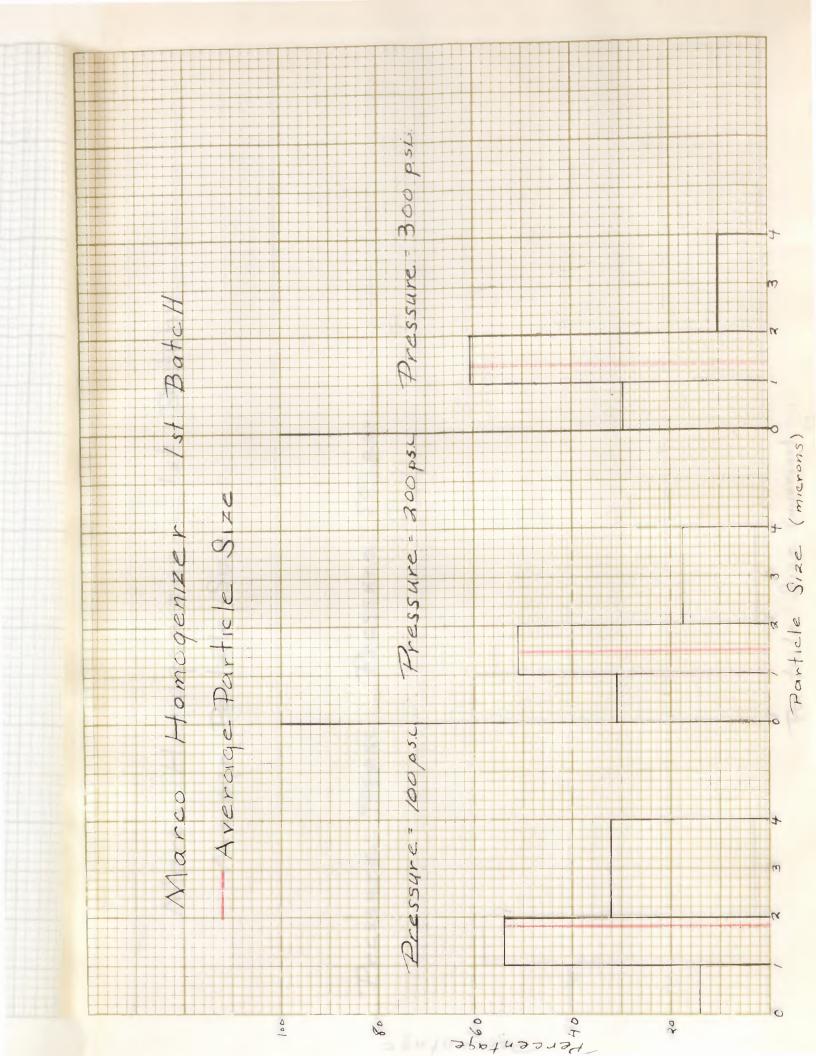
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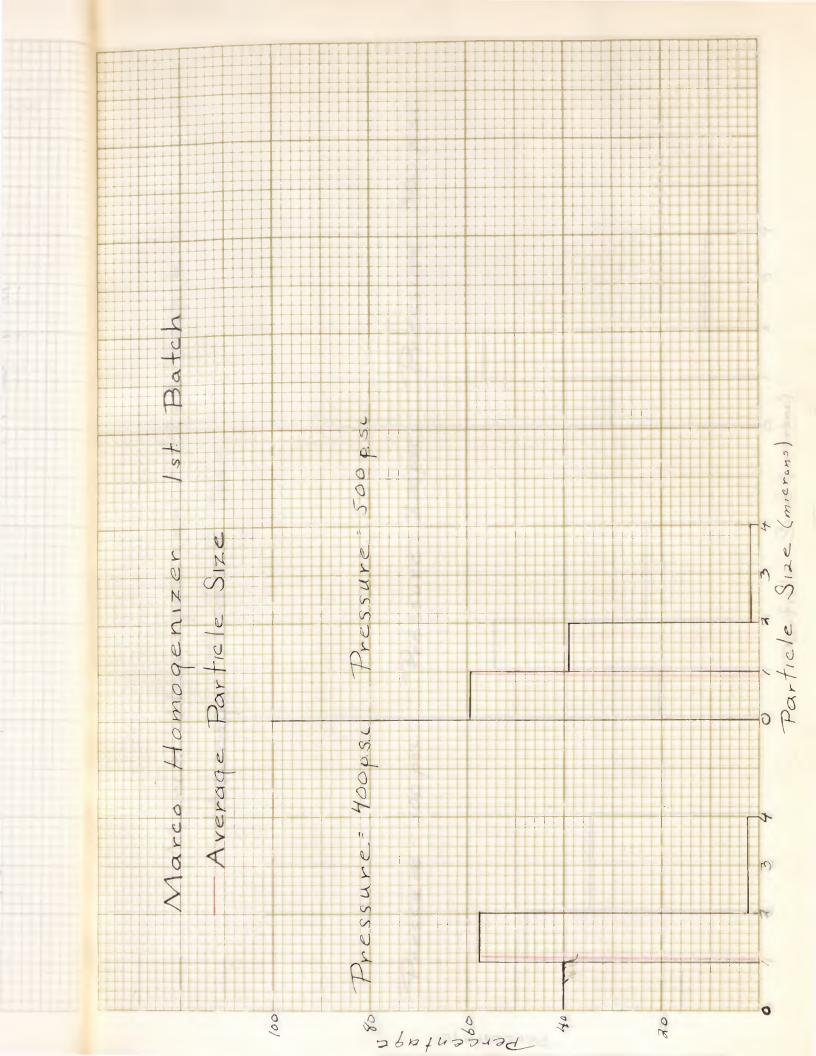
Kraemar and Stamm also report an increase in the number of smaller particles with repeated homogenization.

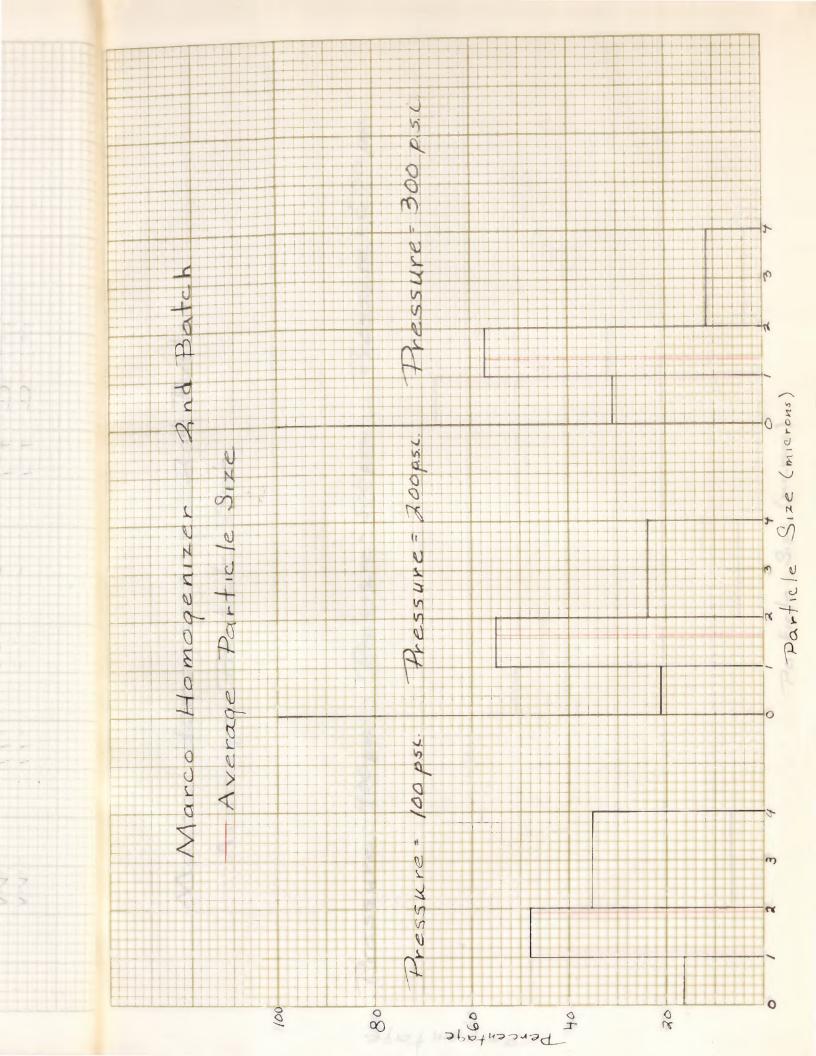
They report that a benzene in water emulsion when stabilized by gelatin and homogenized broke completely. The same emulsion without gelatin did not break after homogenization.

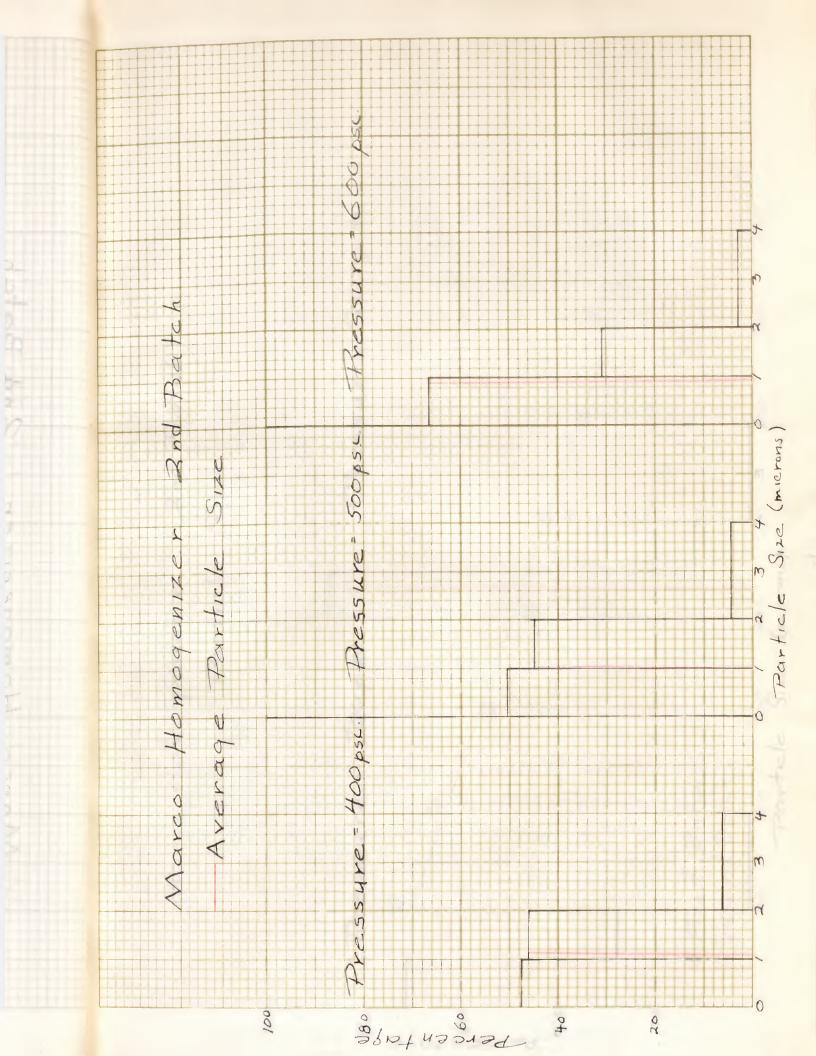
The final particle size of an emulsion passed through a pressure type homogenizer depends upon the following factors:

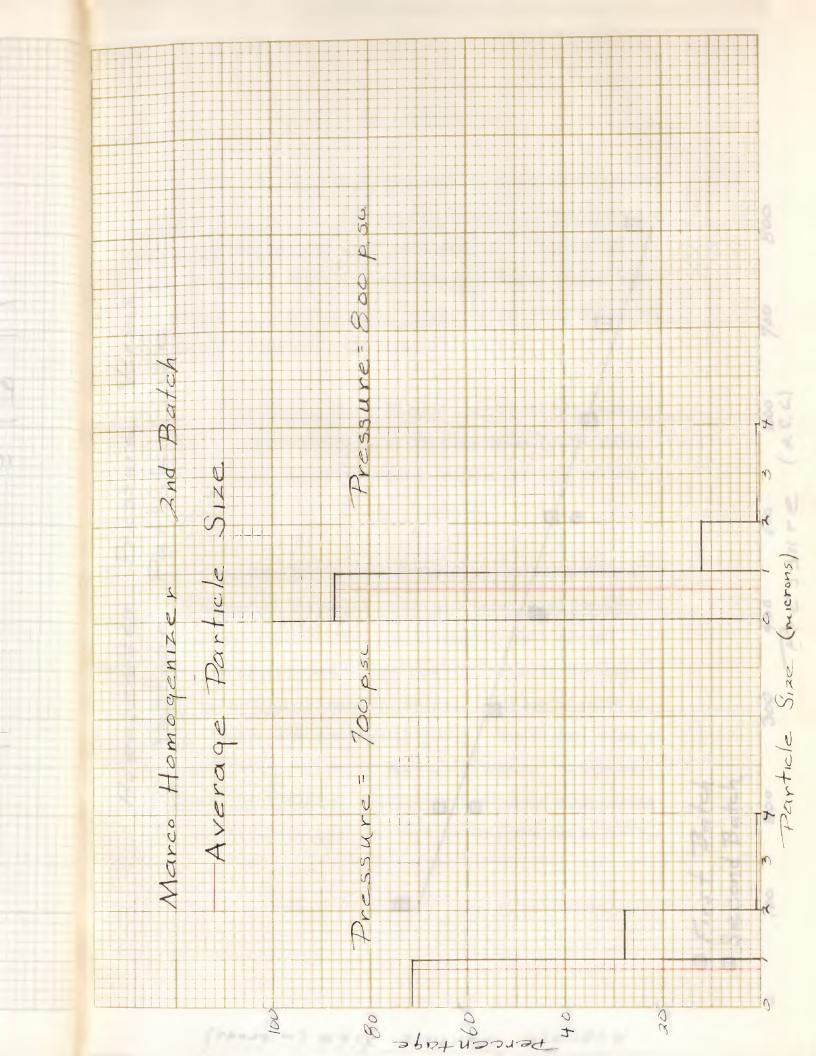
- a. particle size of the feed emulsion
- b. viscosity of the emulsion
- c. pressure of homogenization
- d. type of emulsion.
- (1) Sibree Trans. Faraday Soc. 27, 170, 1931
- (2) Dorey Technical Aspects of Emulsions, Harvey, London, 1935
- (3) Hatschek Kolloid-Z 7, 81, 1910
- (4) Smith and Grinling Quart. J. Pharmacology 3, 354, 1930
- (5) Kraemar and Stamm J. Am. Chem. Soc. 46, 2716, 1924

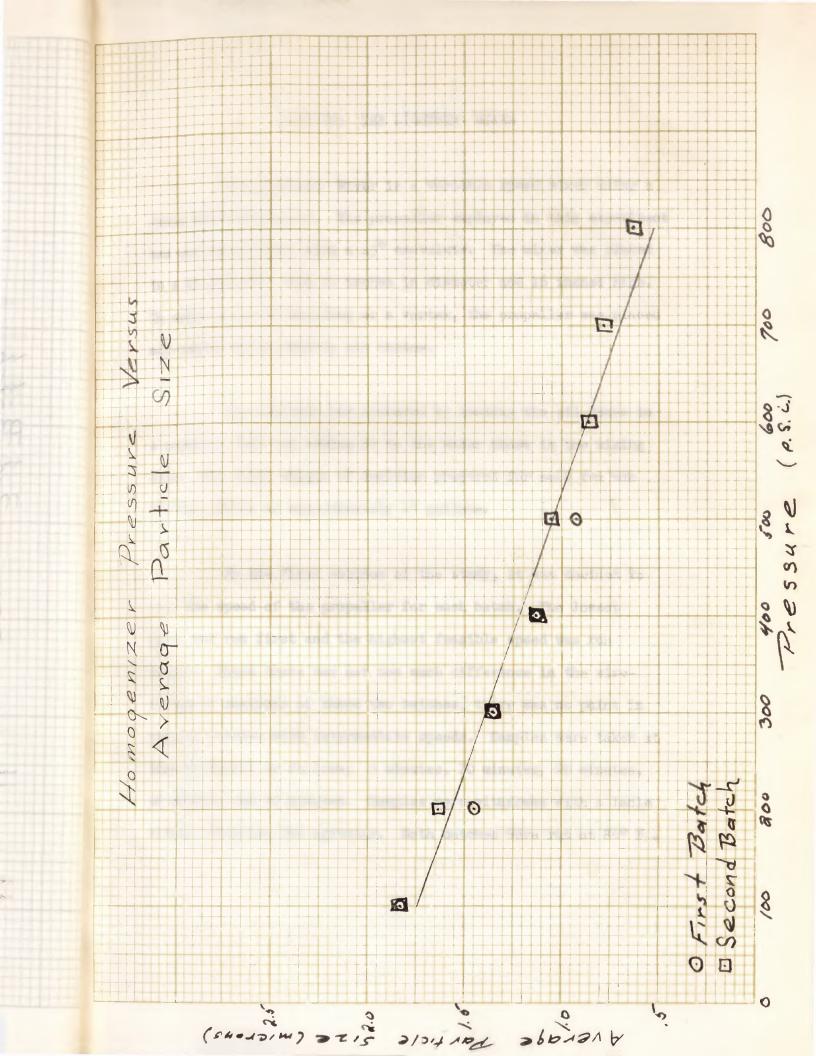












#### PART VI: THE LIGHTNIN' MIXER

The Lightnin' Mixer is a variable speed mixer using a three blade propeller. The propeller employed in this experiment had one inch blades with a 45° convolute. The mixer was placed in a cylindrical tank 21 inches in diameter and 16 inches high. In order to avoid whirling or a vortex, the propeller was placed off-center approximately six inches.

The emulsion was prepared by heating the oil phase in a separate tank and adding it to the water phase in the mixing tank. The total weight of emulsion prepared for each run was 140 lbs. which is approximately 17 gallons.

In the first section of the study, it was decided to vary the speed of the propeller for each batch. The lowest speed was run first and the highest feasible speed was run second. Since there was not too much difference in the size-frequency analysis of these two batches, there was no point in running batches with intermediate speeds. Samples were taken at time intervals as follows; 5 minutes, 10 minutes, 20 minutes, 40 minutes and 90 minutes. Samples were withdrawn with a ladle without stopping the agitator. Both batches were run at 86° F...

The high speed batch foamed after 20 minutes and was possibly aerated. On aging, the 90 and 40 minute samples of the high speed batch separated water before the 5, 10 and 20 minute samples. This indicates that aeration is a detriment to the stability of the emulsion. The use of this type agitator, therefore, should be confined to a speed only as fast as is necessary to move the bulk of the liquid.

Examination of the plot of average particle size versus time of mixing indicates two stages of mixing. In the first stage of mixing, the particle size rapidly decreases with time of mixing. In the second stage of mixing, there is wery little change in the average particle size with time. Mixing beyond the first stage appears to have no advantage and is time consuming. The 130° F. curve has a first stage mixing period of about 20 minutes.

1

Harkins and Beeman using a high speed drink mixer report that 20 minutes stirring gave the same distribution of sizes that ten minutes of stirring produced. It would appear from their report that the mixing apparatus employed by them was much more violent than the one used in this experiment.

Expectations would be, therefore, that the first stage of mixing would be much shorter. The first stage of mixing is probably accomplished during the first ten minutes as their data indicates.

2

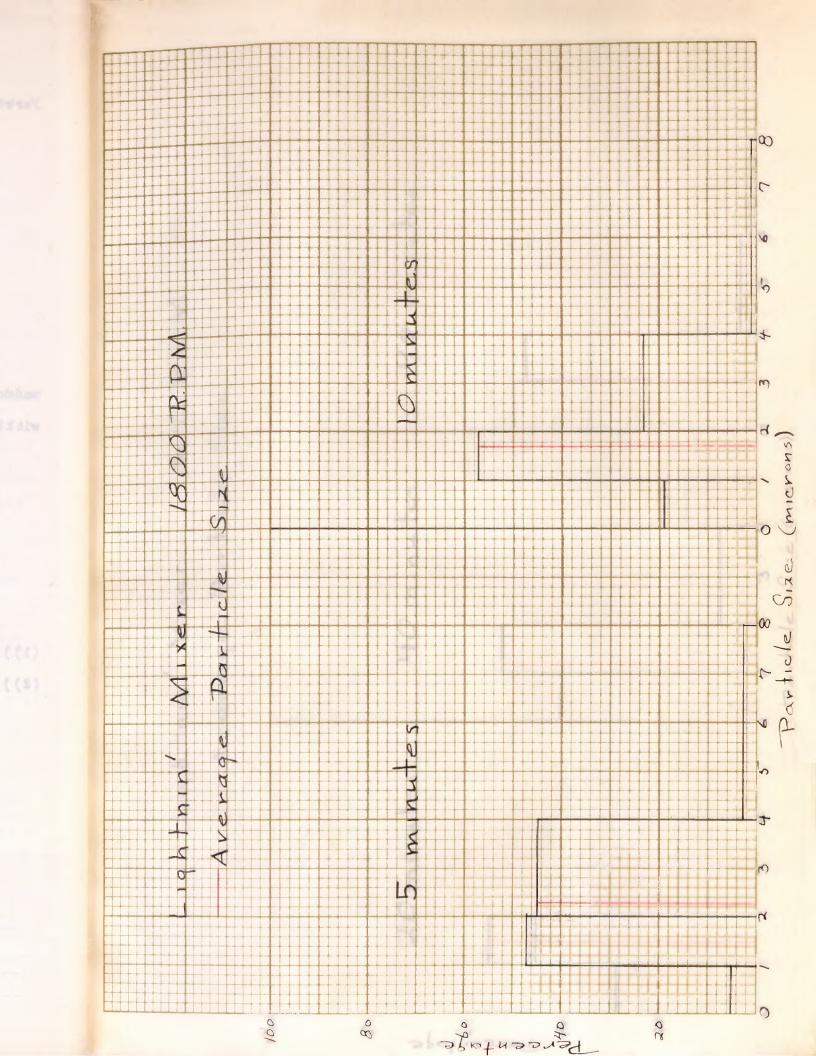
Dorey reported size-frequency analysis of emulsions made with a Beach Mixer. He did not report any variation with time. His emulsions were mixed for ten minutes.

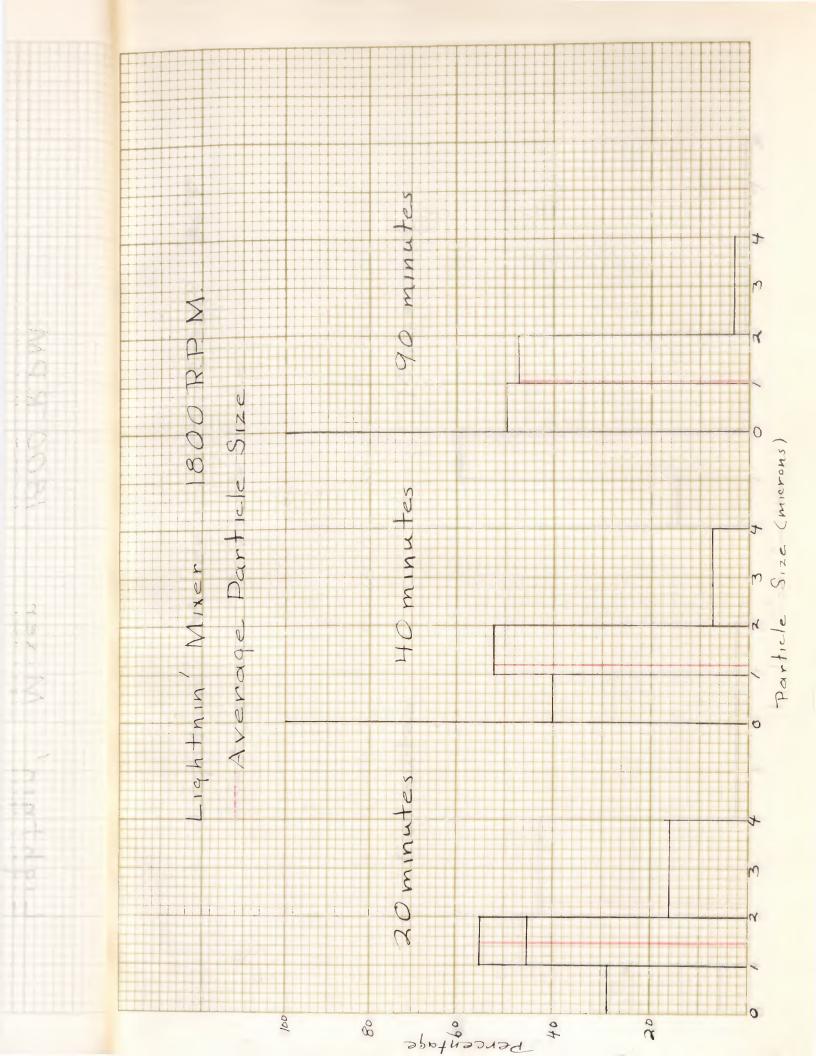
- (1) Harkins and Beeman
- (2) Dorey

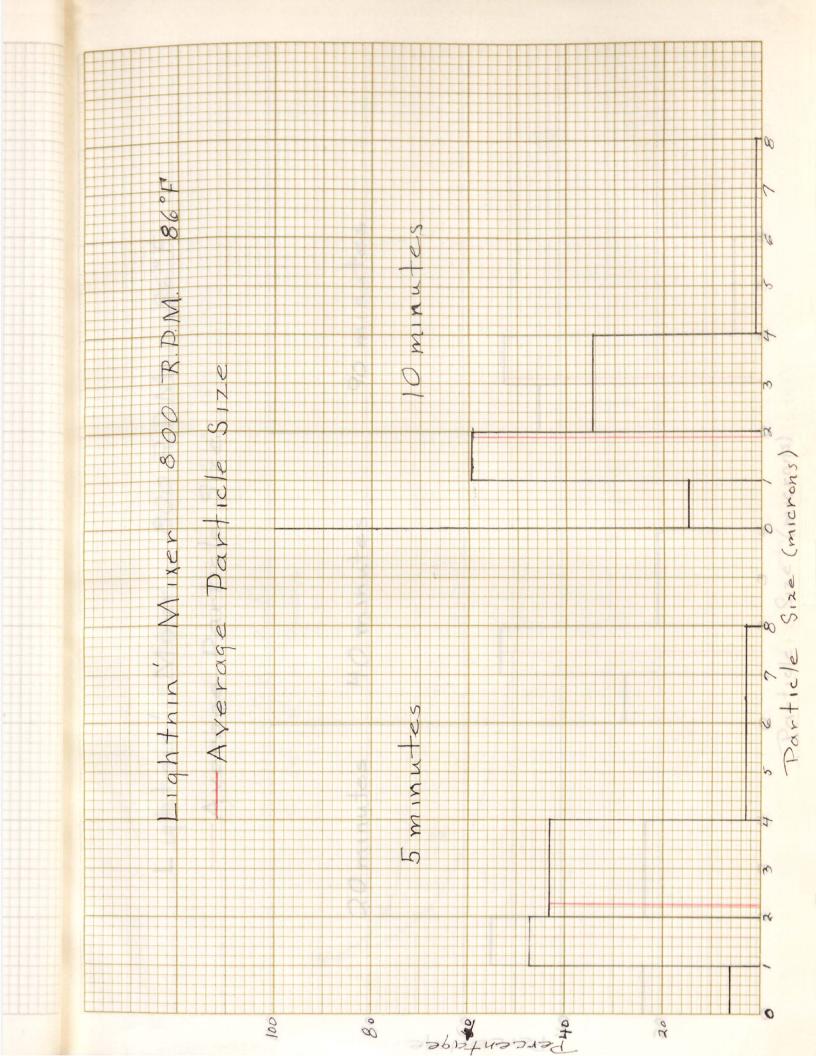
J. Am. Chem. Soc. 51, 1688, 1929

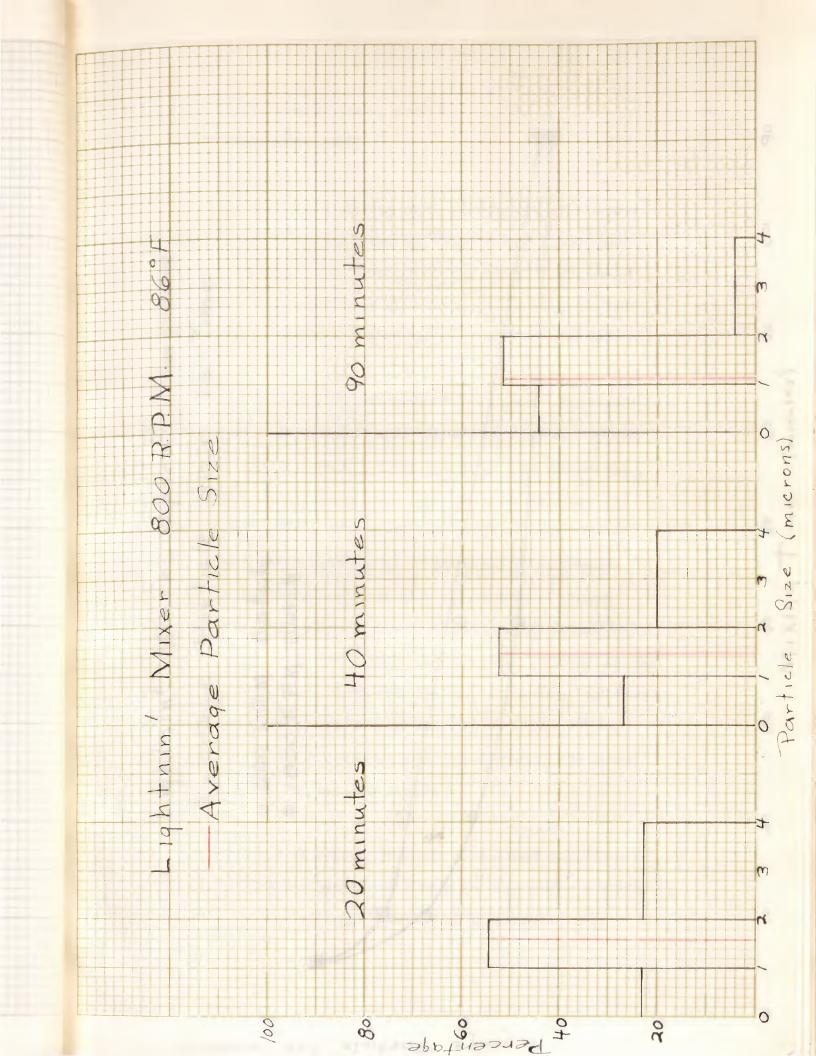
Technical Aspects of Emulsions,

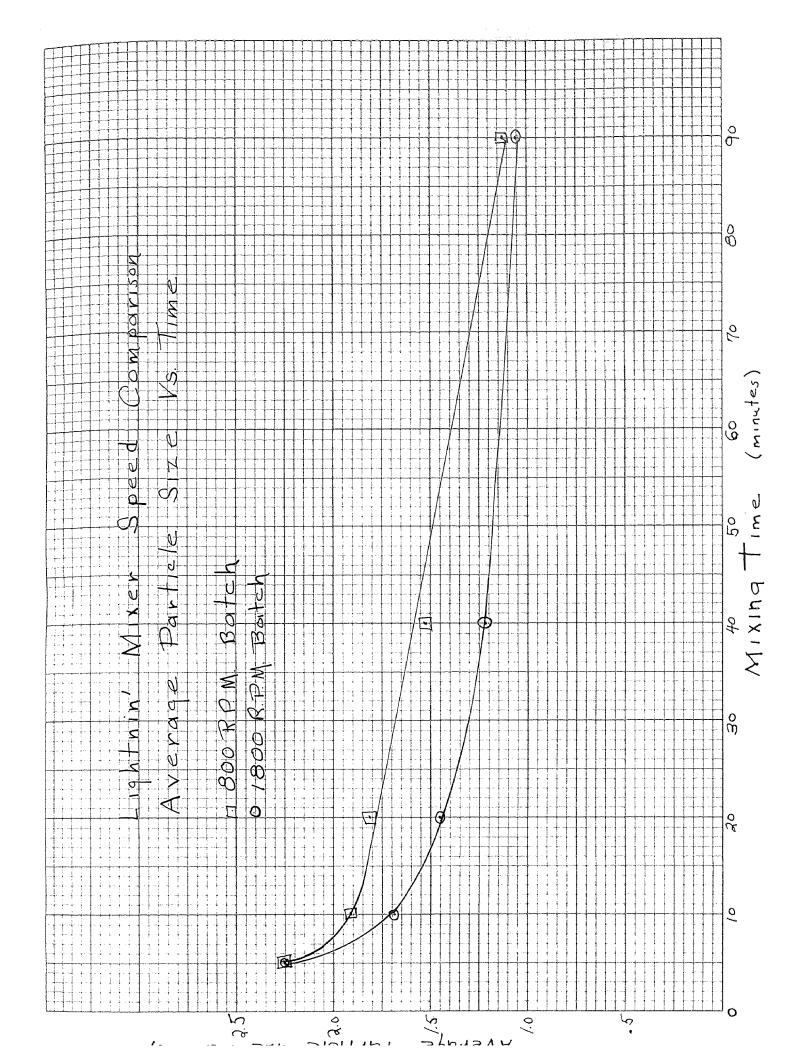
Harvey, London, 1935











Part VI: The Lightnin' Mixer, Cont'd:
Temperature Study

In the second section of this study, it was decided to vary the temperature and operate the mixer at a low speed (approx. 800 R.P.M.). In addition to the 86° F. batch prepared in the first section of this study, three other batches were prepared at temperatures of 190° F., 160° F., and 130° F.

The samples taken from the three higher temperature batches started to separate water immediately. After one day, the amount of water separation was measured. The precentage separation varied inversely with time and temperature as may be seen in the graph of percentage separation versus time of mixing. The striking similarity of the plots of percentage separation and average particle size versus time of mixing would indicate that particle size was an important factor in this separation. The 86°F. batch, however, had a larger average particle size than the 130°F. and the 160°F. batches; but there was no marked water separation of the samples of the 86°F. batch. While particle size may be a factor causing the water separation, it is not the only cause.

The plot of average particle size versus temperature is U shaped for short periods of mixing and approaches a straight horizontal line for prolonged periods of agitation.

Part VI: The Lightnin' Mixer, Cont'd:

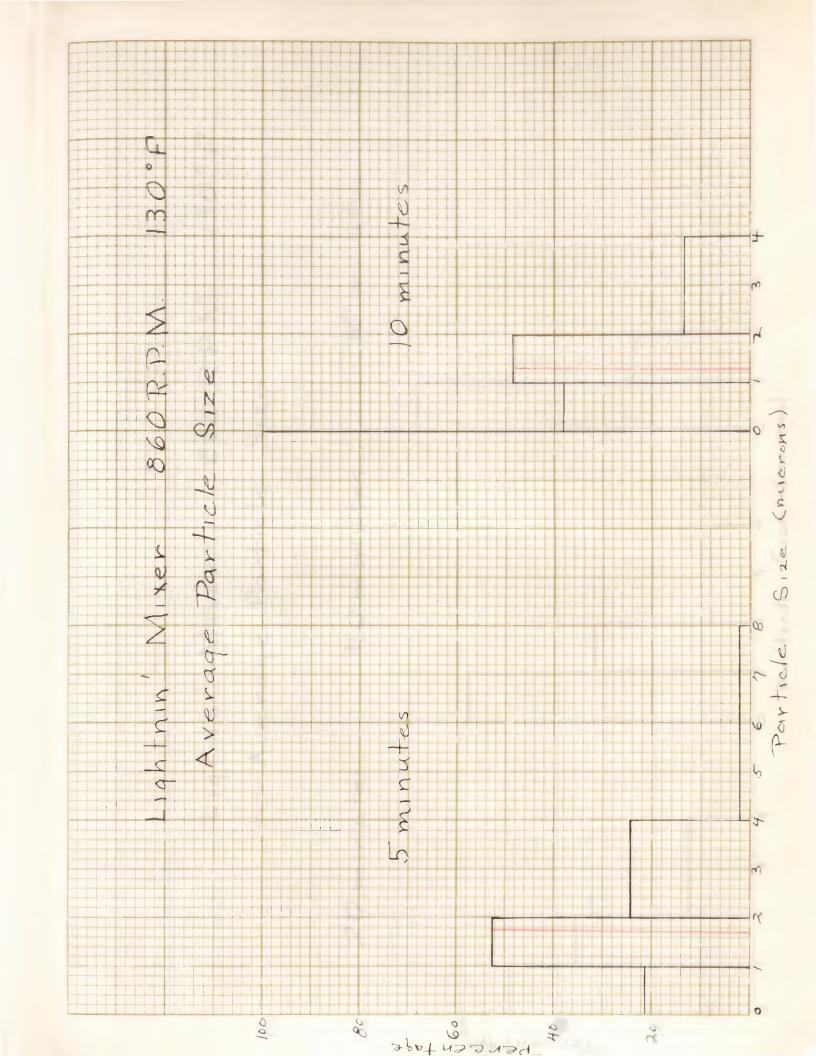
(Temperature Study)

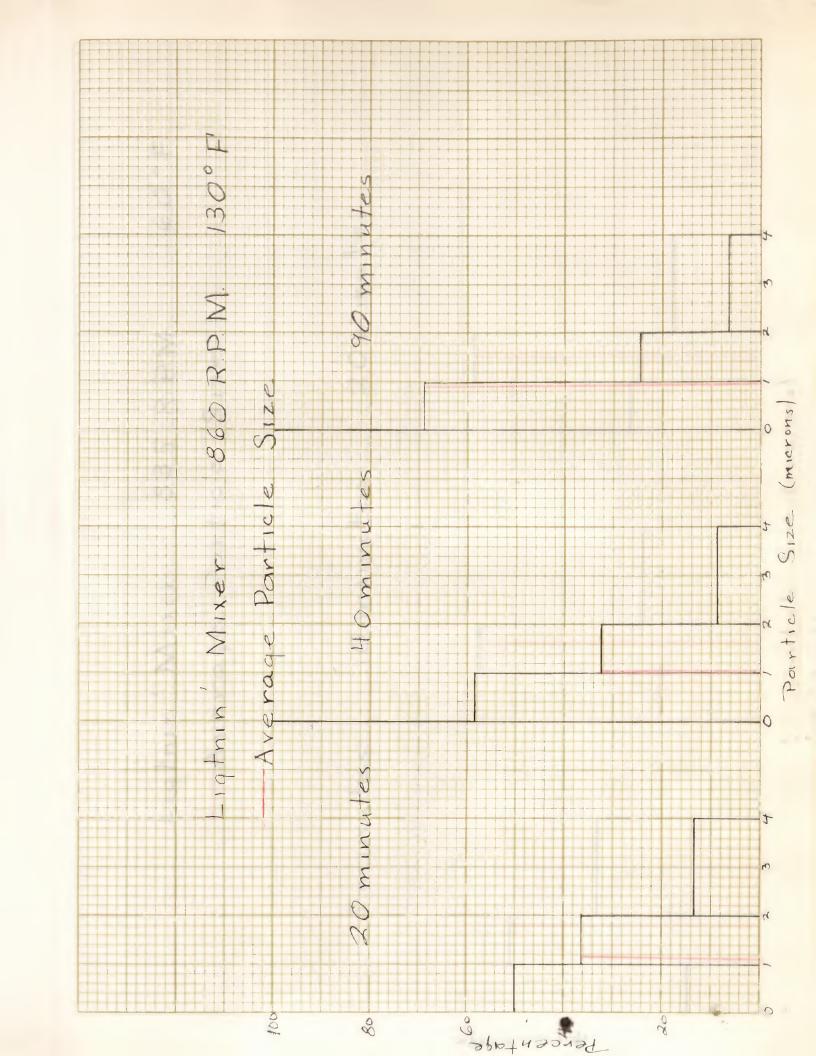
As regards particle size, there appears to be an optimum temperature of mixing, about 130° F., for this emulsion. Prolonged mixing, however, overcomes the advantage gained at the optimum temperature. It may be noticed from the plots of average particle size versus time of mixing that the higher temperature curves (190°F., 160°F.) have a longer first stage of mixing.

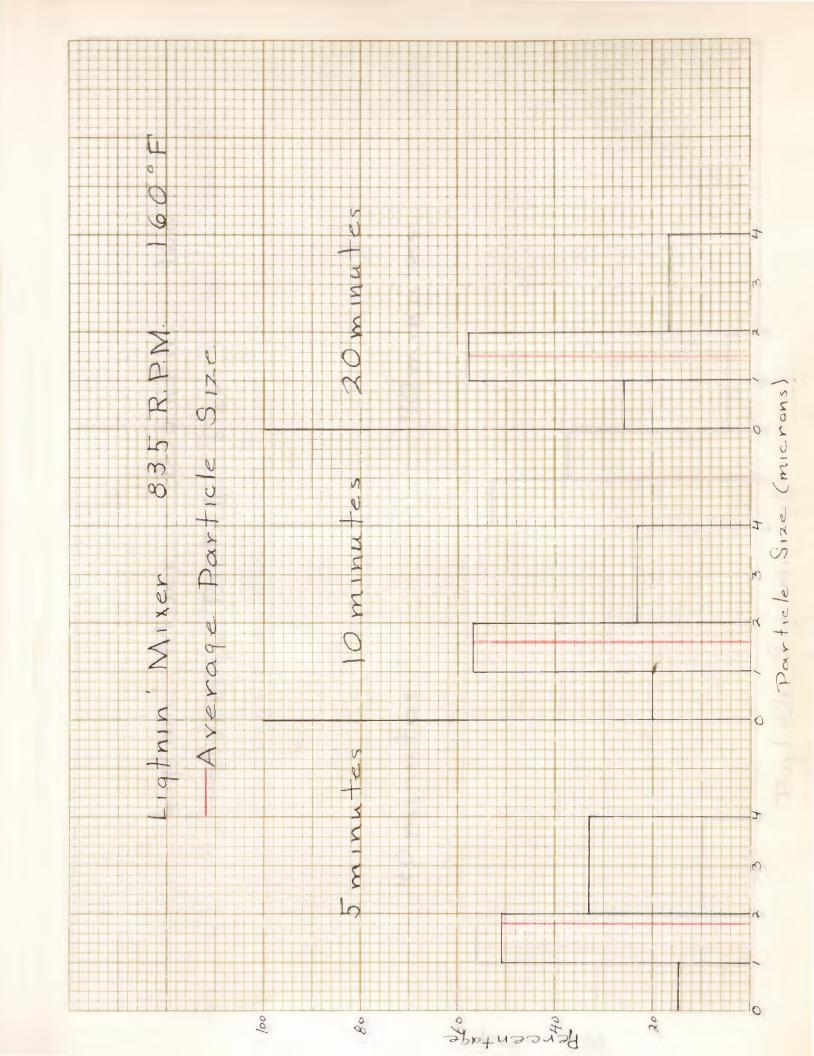
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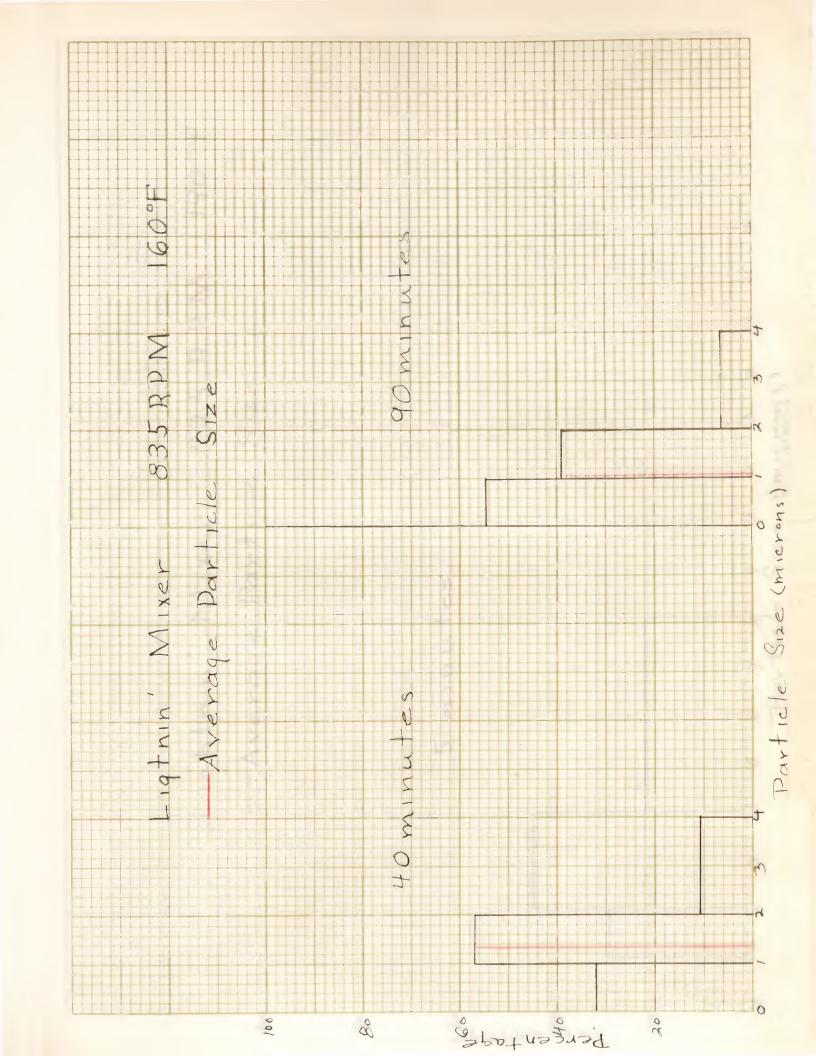
Woodman reported that emulsification of toluene was greatly facilitated by the higher temperature. In his work, he used sodium cleate and investigated a temperature range of  $20^{\circ}$  C. to  $60^{\circ}$  C..

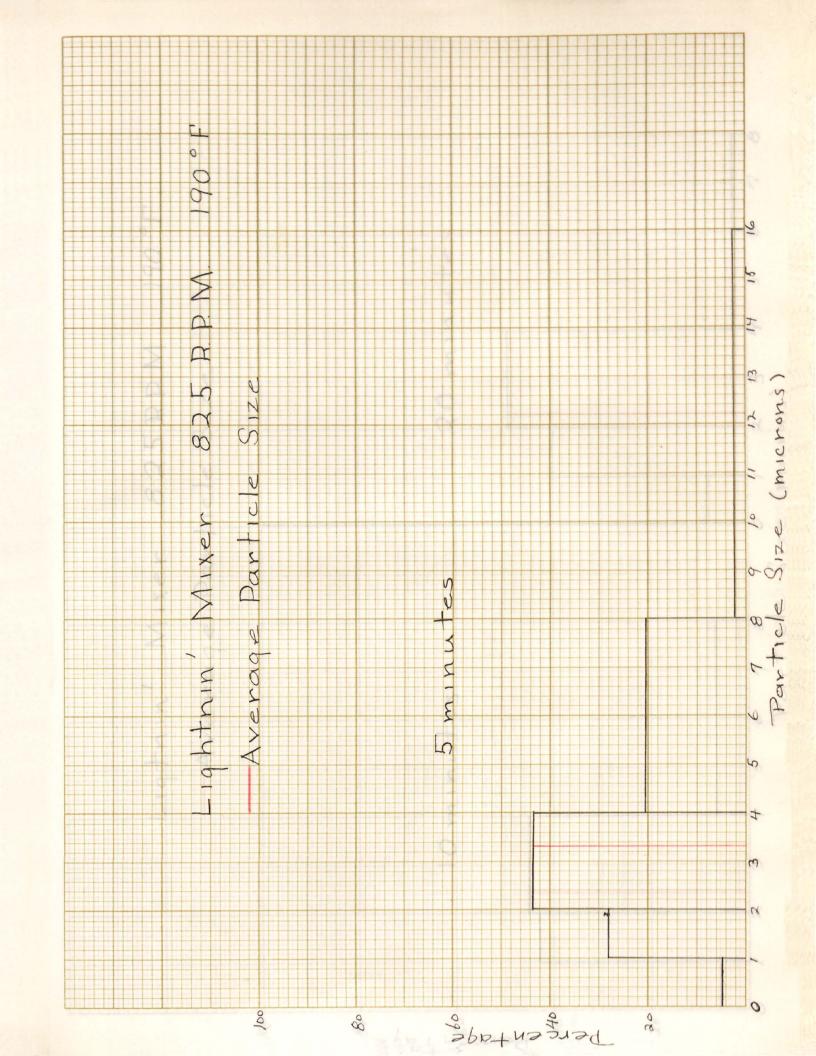
(1) Woodman J. Agric. Science 17,55, 1927

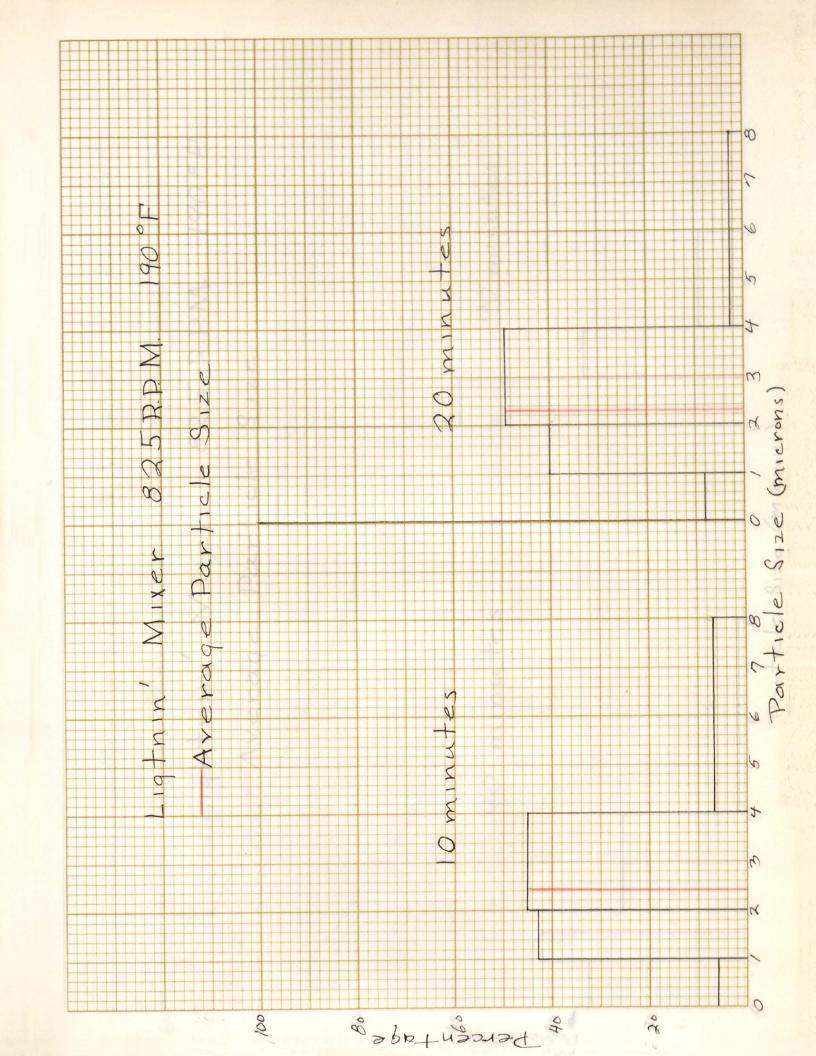


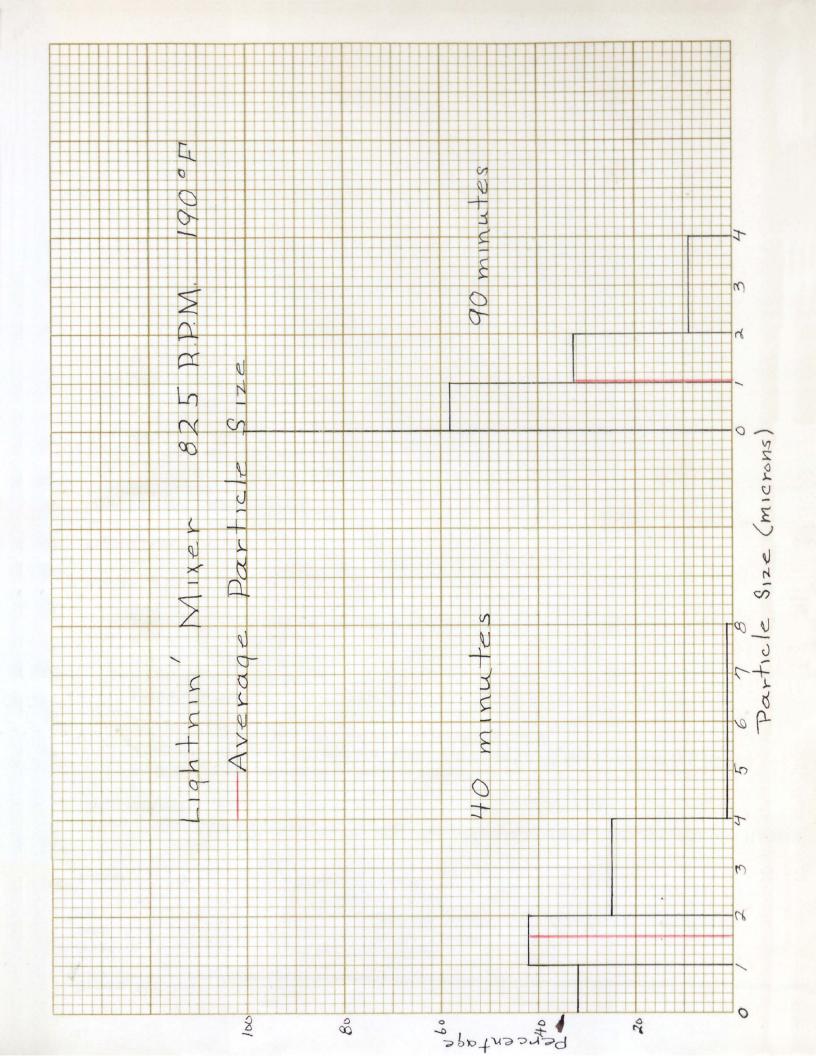


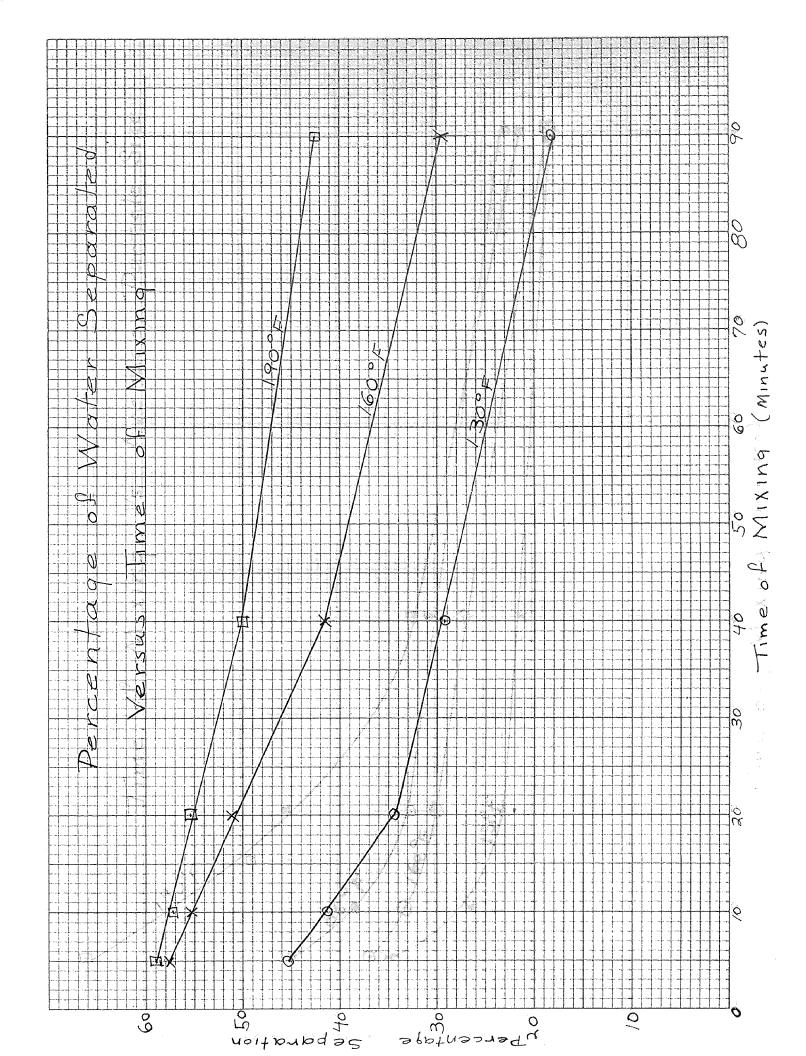


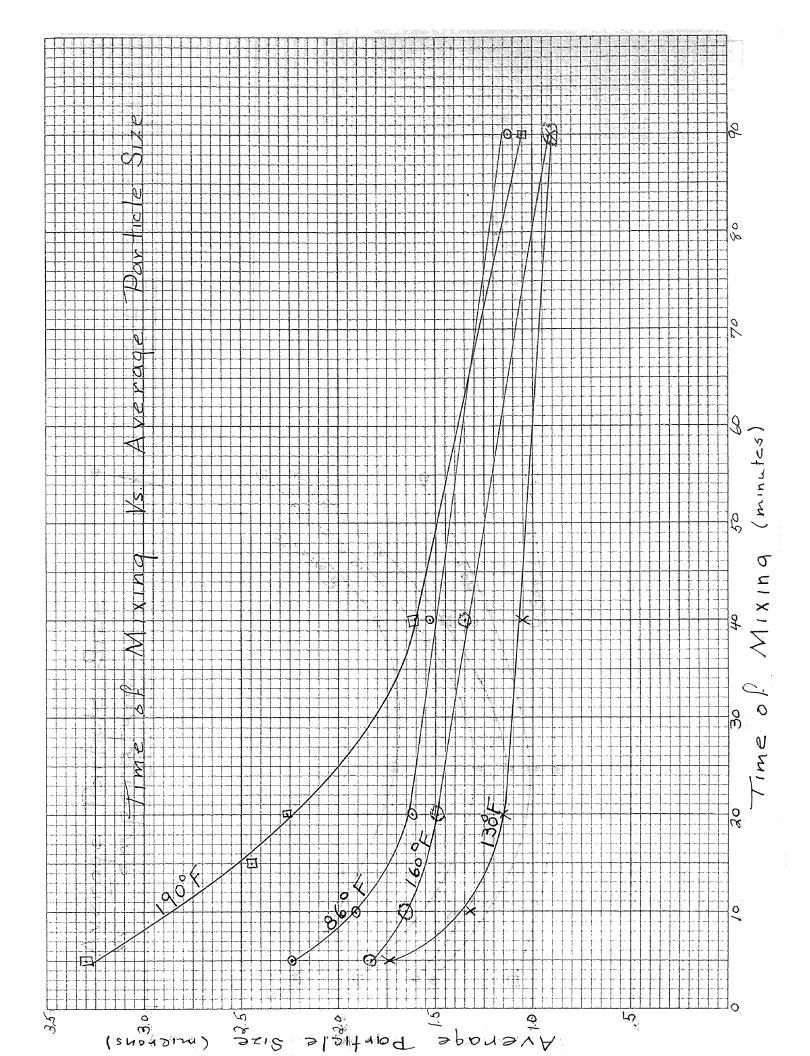


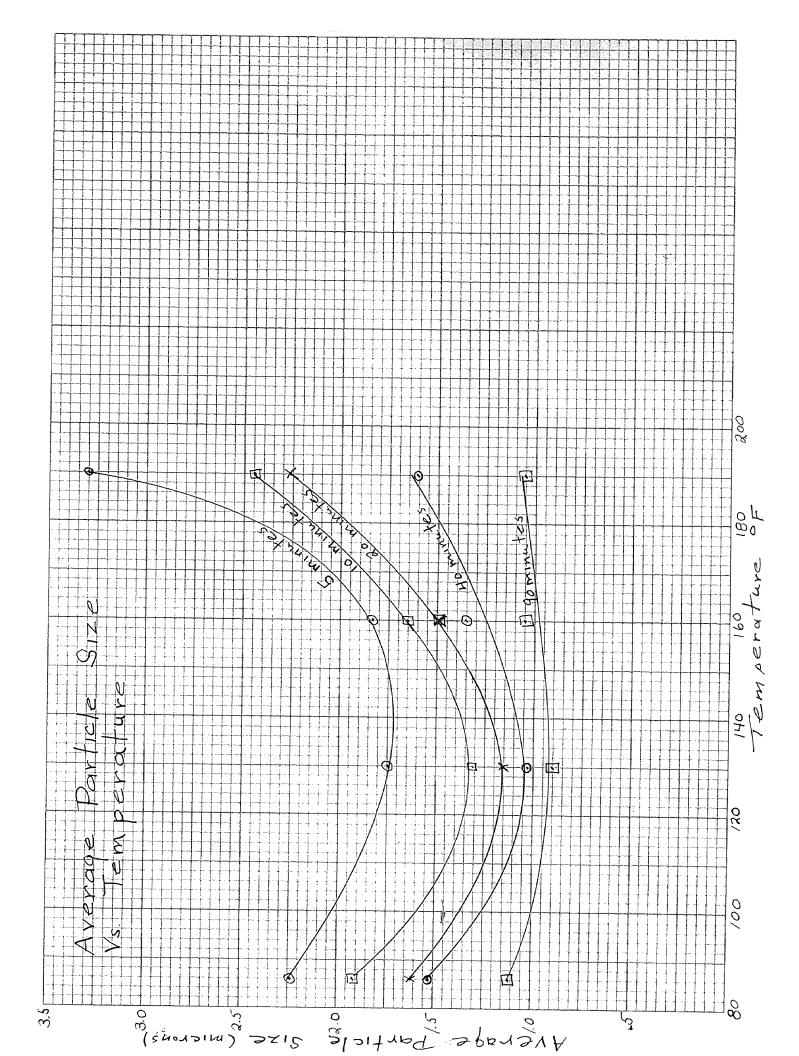












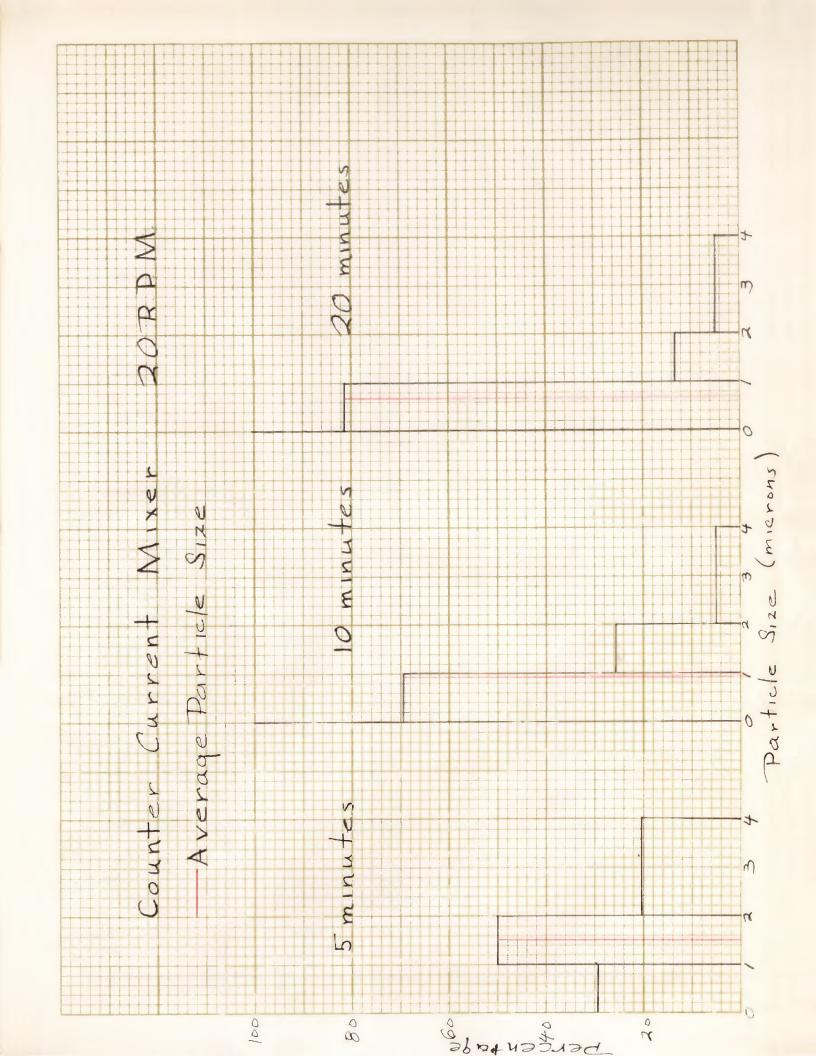
#### PART VII: THE COUNTER CURRENT MIXER

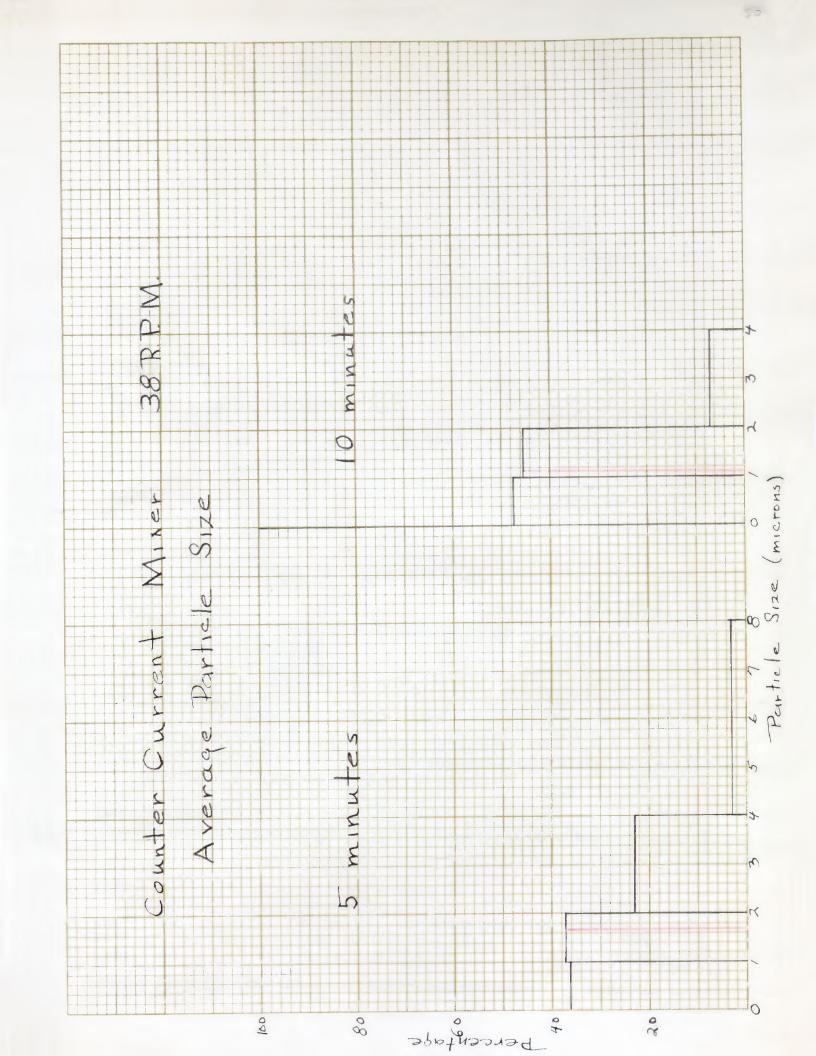
The counter current mixer is a slow speed mixer with a large paddle area. The mixer consists of an inner agitator, comprised of four two inch wide blades set at an angle of 45°, and an outer scraper which brings the emulsion into the center of the tank.

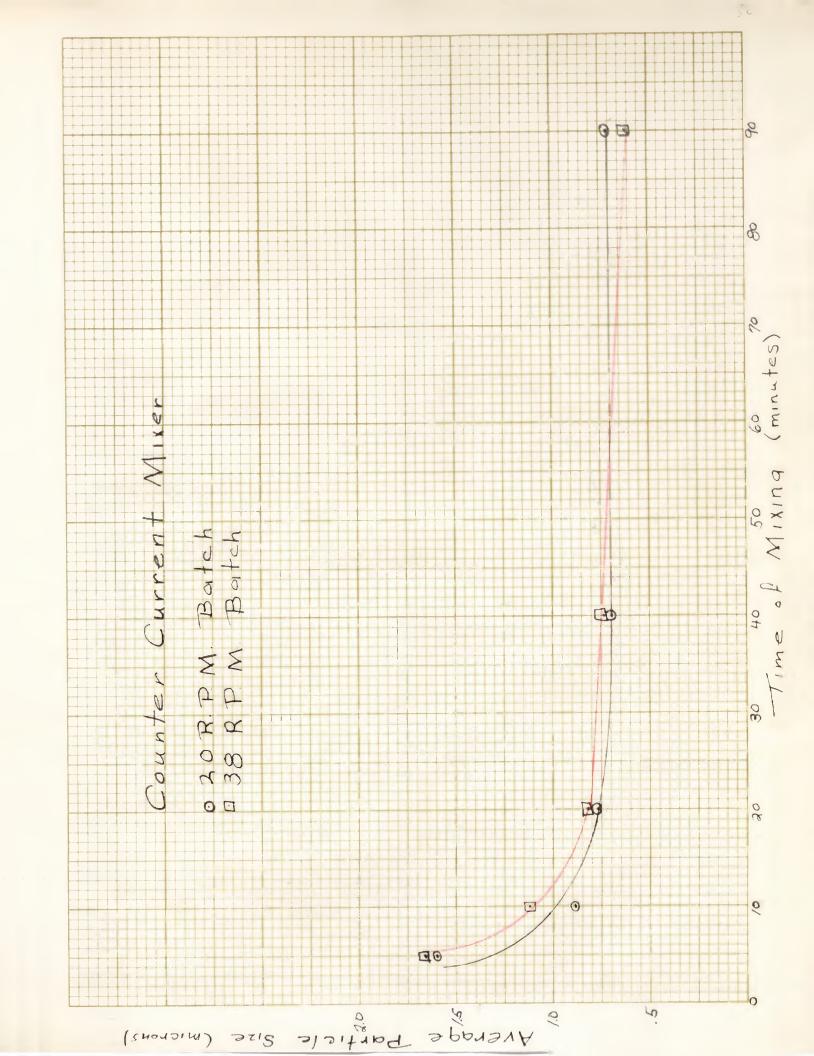
The inner agitator and outer scraper rotate in opposite directions. This mixer was used in the same tank as the Lightnin' Mixer and the same volume of emulsion was also prepared. Two runs were made; a low speed run of 20 R.P.M. and a high speed run of 38 R.P.M.. There was no material decrease in particle size at the high speed in comparison with the low speed. Samples were taken at 5, 10, 20, 40 and 90 minutes. The samples were removed with a ladle after the agitator was stopped, but while the mass of liquid was in motion.

The average particle size of each sample was calculated by multiplying the percentage of each size group by the mean particle size of the group and dividing by 100. A plot of average particle size versus time of mixing indicates that after 20 minutes of mixing the average particle size approaches a minimum and further mixing does not appear to decrease the particle size.

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#### PART VIII: EMULSION AGING DATA

Samples of the emulsion were stored in a constant temperature room at 70° F.. The samples were examined daily for signs of separation. The only separation noted during a two month period was small amounts of water in most of the samples. This separation occurred erratically and could not be correlated with particle size. In some cases, the separation occurred first in the samples that were most aerated, such as the 90 and 40 minute samples of the Lightnin' Mixer 1800 R.P.M. batch. Aeration, however, does not completely account for the erratic water separation in other batches. The first homogenizer batch is a typical example. The 300 p.s.i. sample had water separation after 24 hours while the other samples did not separate for six weeks. The counter current mixer batches did not show any separation.

It is important to note then that the other emulsifying mechanisms were localized in nature. While all the
mechanisms satisfactorily reduced the oil particle size, it
might well be that the counter current mixer was the only
mechanism to evenly disperse the oil droplets throughout the
mass of the water. This would bear further investigation with
special regard to the small blade high speed mixing apparatus.

It may be that the high speed mixing apparatus dispersed the oil
droplets satisfactorily but incorporated an undue amount of
air in the emulsion.

Part VIII: Emulsion Aging Data, Cont'd:

The 5, 30 and 160 micrometer setting samples of the colloid mill and the 100 and 500 p.s.i. samples of the first homogenizer batch were checked for particle size growth. For the first week, the samples were examined daily. For the remainder of a two month period, the samples were examined weekly. There was no change in the average particle size of the emulsions examined during the two month period.

The purpose of this study as stated in the introduction was to propose a method of preparing the optimum commercial emulsion.

Most of the present day homogenizers and colloid mills require a predispersion of the emulsion. The high speed propeller mixer and the slow speed paddle mixer represent two possible predispersing mechanisms. In this study, the slow speed paddle mixer had three definite advantages. There is less danger of undesirable aeration with the slow speed mixer. The slow speed mixer produced an emulsion with a smaller average particle size in a shorter length of time than the high speed propeller mixer. The slow speed mixer should then be used as the predispersing mechanism. To determine the mixing time, a plot of average particle size versus time should be constructed for the mixing system to be used. The time will be determined by the length of time necessary to complete the first mixing stage. For the particular slow speed mixing system used in this study that time was 20 minutes.

In this study, it was discovered that there was an optimum temperature of mixing as far as the particle size is concerned. The literature indicates that the effect of temperature varies from emulsion to emulsion, therefore this will have to be determined for the particular emulsion desired.

The next problem is the choice of the final dispersing mechanism. The colloid mill and the pressure homogenizer are both good dispersing mechanisms. There is only one basis for choice between them and it may be a poor one. Many investigators have reported that repeated pressure homogenization further reduces the particle size of the dispersed phase. This would indicate that the final particle size of the homogenized emulsion varies directly with the particle size of the feed emulsion.

No reports of this nature have been made for the colloid mill.

In order to take full advantage of the initial dispersion, the pressure homogenizer should be used as the final dispersing mechanism. The pressure used should be as high as possible.

The average particle size decreases with increasing pressure.

If a stabilizing gum is to be incorporated in the emulsion, it might be better to add the gum after homogenization than before. Two disadvantages are encountered with the addition of gums before homogenization. First the increased viscosity of the emulsions decreases the efficiency of the homogenizer. Secondly, there have been reports of gum stabilized emulsions breaking immediately after homogenization while the same emulsion without the gum did not break after homogenization.

#### PART X: REPORT ON LITERATURE SEARCH

A literature search was conducted to gather the published information concerning emulsions that relates to this study.

A search of the chemical abstracts was conducted in the following manner:

- a. The indexes were examined for related articles under emulsions, emulsification and particles.
- b. The abstracts of the articles selected from the indexes were read to determine the relation ship of the article to this study.
- c. After reading the abstracts, the articles that were related to this study were read.

The search as outlined above follows:

Part X: Report on Literature Search, Cont'd.

Articles selected from index 1950, 1949, 1948 and 1947:

## 1950

	1950	
Page of abstracts read:		Titles and source of articles read:
4 f		
880 i		·
4296 e		
10389 g		
404 <b>c</b>		
404 d		
10448 a		The Formation & Flow of Emulsions
		J. Colloid Science 404-13 1950
3670 i		Soap, Perfumery & Cosmetics 1949
		Pg. 1338-40
	1949	
6202 i	in <del>, majaga di</del> estus	
4266		
	1948	
1750 f		Mfg. Chemist 18 494-9 1947
	1947	
4015 h	and the same of th	
4344 b		
1133 h		
5759 <b>f</b>		

Part X: Report on Literature Search, Cont'd.

# Articles Selected from Index 1937 - 1946

Page of abstract read	Titles and source of article read
34-653-1	
33-9697-6	
31-2877-9	
31-5227-6	
35-5355-6	Vaprosy Pitanya 7 No. 6 60-80 1938
36-218-2	
33-5263-2	
37 <b>-</b> 36 <b>43</b> -5	
31-3747-8	
33-9051-9	
37–2635–5	
35–2392–5	
32–3230–5	Size Frequency of Emulsion Particles
	J. Soc. Chem. Ind. 56-447-53 T 1937
34-8073-1	Vaprosy Pitanya 8 No. 4 50-7 1939

Part X: Report on Literature Search, Cont'd.

## Articles Selected from Index 1927 - 1936

# Abstracts read

Articles read

26-902-3

25-4396-5

21-675-9

24-3405-1

25-4155-6

28-3961-9

29-3895-1

22-834-1

25-1423-1

27-3377-5

1917 - 1926

17-3114-8

13-680-4

20-3611-6

16-337-1

19-761-1

19-2447-8

19-2768-3

16-3418-9

1907- 1916

1-2955-8

1-2961-2

10-274-2

5-619-1

### Part X: Report on Literature Search, Cont'd.

After a search of the chemical abstracts, several books on emulsions and colloids were examined. Below is a list of books selected for references:

Bancroft "Applied Colloid Chemistry"

Bennett "Practical Emulsions"

Clayton "The Theory of Emulsions and Their

Technical Treatment"

Harvey "Technical Aspects of Emulsions"

McBain "Colloid Science"

Thomas "Colloid Chemistry"

Travis "Mechano Chemistry and the Colloid Mill"