



A METHOD OF  
EMULSIFYING OILS WITH DIFFERENT  
EMULSIFIERS

THESIS FOR THE DEGREE OF M. S.

G. C. Applebee

1934

Emulsions  
Oils + fats



A METHOD  
of  
EMULSIFYING OILS WITH DIFFERENT EMULSIFIERS

A Thesis Submitted to the Faculty  
of  
Michigan State College

In Partial Fulfillment of the  
Requirements for the Degree  
of  
Master of Science

By  
G. C. Applebee  
1934

TS41

AG48

I wish to take this means of expressing my appreciation to Dr. D. T. Ewing, whose supervision and counsel brought about the attainment of this thesis.

## Contents

|              | <u>Page</u> |
|--------------|-------------|
| Introduction | 1           |
| Experimental | 4           |
| Apparatus    |             |
| Procedure    |             |
| Results      | 8           |
| Discussion   | 14          |
| Summary      | 17          |

## Introduction

In this thesis, the object is to present a general method of emulsifying all types of oil. It is true, that the emulsification of each oil is an individual problem and by practice and patience this general method can be improved upon giving greater stability for that particular oil.

"An emulsion is a system containing two liquid phases one of which is dispersed in the other." Hatscheks Foundation of Colloidal Chemistry. Holmes states that "Emulsions are dispersions of minute drops of one liquid in another."

From the standpoint of emulsifying oils in water we can say an emulsion can be described as the combination of the desirable properties of both oil and water. In order to obtain this combination a third and fourth material is added which will be called an emulsifier. In the course of experimentation, glue, rosin, skimmed milk, cocoanut oil plus arabic gum, cotton seed oil with arabic gum,

oelic acid with arabic gum, in all cases emulsions were formed but their stability varied.

The emulsifier has a two-fold purpose.

(a) the forming of an emulsion.

(b) to give stability.

An excellent way of determining the type of emulsion devised by Briggs J Physical Chemistry 18-34 (1914) stated briefly--If a film of an emulsion of oil and water be examined under a microscope, a liquid medium will be formed and suspended in that medium small droplets of the second will be found. If the medium is oil and the droplets are water, it would be a water in oil emulsion. If the medium is water and the droplets are oil, it would be an oil in water emulsion. An oil in water emulsion can be readily diluted with water, while a water in oil type can only be diluted with oil. However, one can be changed into the other by the addition of .8 grams of Damar Gum to each liter of the emulsion.

The properties of an emulsifier are of a two-fold nature:

(a) the drops shall be so small that they will remain suspended.

(b) a viscous film or coating should encase each drop to prevent coalescence.

In order to secure a fine division of the dispersed liquid homogenizing as well as mechanical agitation is required during the preparation of the emulsion.

Clowes J Phys. Chem.--20-403 (1916) states that an acid or a salt of a fatty acid added for the following reasons

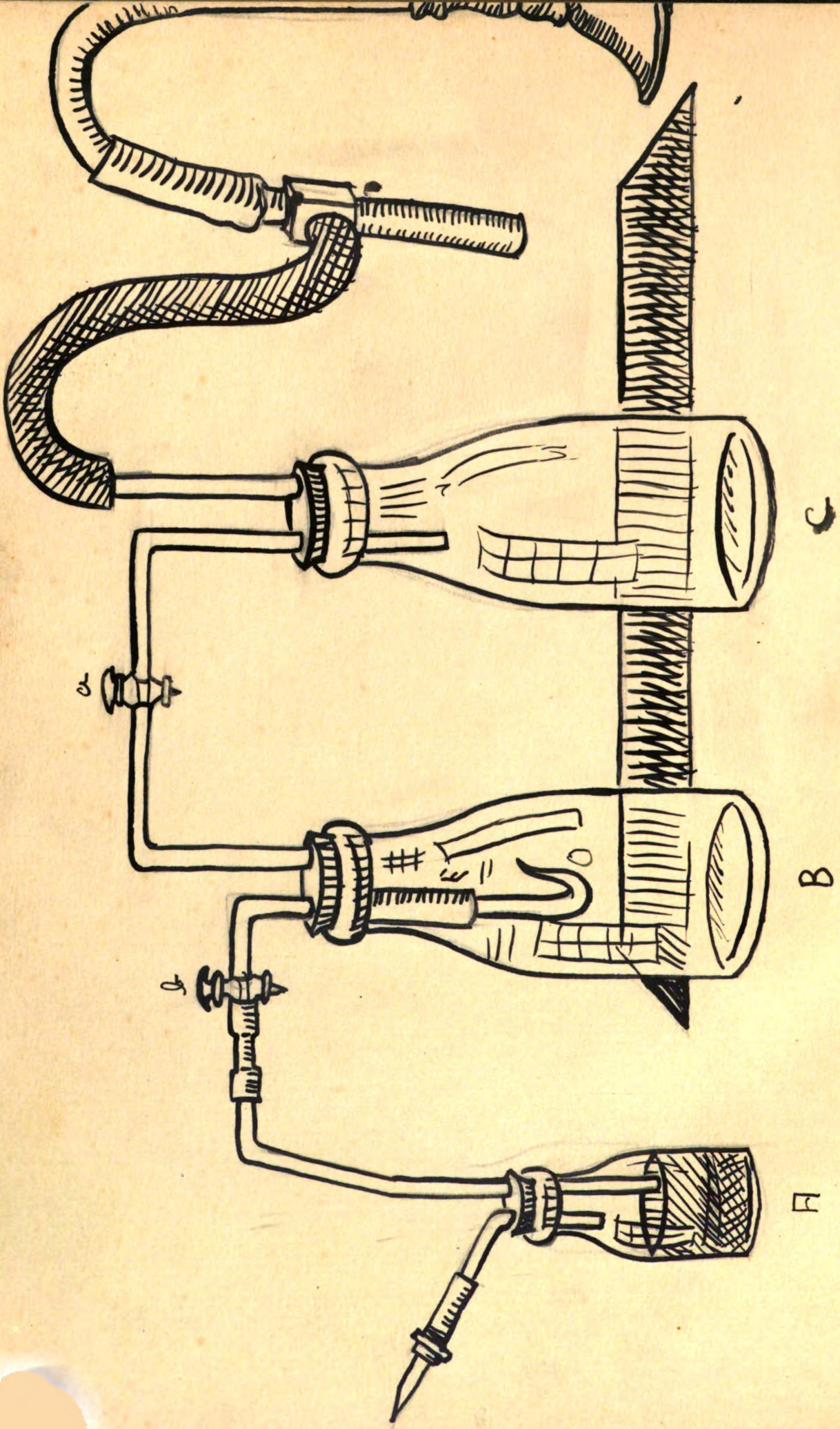
1. To lower the surface tension so that the fine spherical drops will be easily formed and will have a small tendency to recombine.

2. A film is provided around each drop and this film separates each particle from the other, preventing coalescing.

The substances used in this process are four in number.

- (1) The oil to be emulsified
- (2) Water
- (3) Oelic Acid
- (4) Arabic Gum

The oelic acid used is an ordinary C.P. product.



The arabic gum was of the C.P. grade and always before using "degreased" by grinding in ethyl alcohol for five minutes, then grinding in petroleum ether. Krantz and Gordon Colloid Symposium Monograph found that petroleum ether treatment of the gum increases the stability.

For the emulsification of vegetable oils that would be used for food products, cotton seed or cocoanut oil with Arabic gum, using ethyl alcohol alone as the degreaser was substituted.

### Experimental

#### Apparatus

In the homogenizer (Fig. 1), A and B are one-quart milk bottles while C is a two-quart milk bottle, glass tubing fused on to a stop cock connected to bottles A and B. In the same manner B is connected to the two-quart milk bottle C. The bottle C is then connected by rubber tubing to the vacuum pump. Oil is drawn to a fine capillary tube. It was found to be advantageous to have the capillary tube removable from E. Small particles of arabic gum often lodge in the fine capillary and more difficult to remove if tube E is constructed in

a single unit.

#### Procedure

The emulsion was poured in the reservoir A, stop cock (a) being closed; then the stop cock was opened and bottle B was evacuated as much as possible. Then stop cock (a) was opened and the emulsion will pass through. When bottle A was empty, valve (b) was closed and A and B was interchanged, then repeated.

The purpose of the capillary tube is two-fold:

- (a) The small capillary reduces the size of the globules.
- (b) The globules in turn are hurled against the sides of the flask. This seems to aid in emulsification.

An ordinary drink mixer can be used for an agitator. An improvement can be made to a great advantage by using two thin discs with four radii cuts turned up in propellor fashion. One of these discs was placed on the end of the stirrer and the second disc placed three inches above the first.

Bancroft (Applied Colloid P. 357 Second Edition) calls this method the "Soap Method."

It can be used to emulsify the majority of mineral and vegetable oils. With this method all of the oils used did not show a separation within two days. Furthermore dilution with water withstood separation.

In general, the composition of the emulsion studied was as follows:

85 parts of oil (by weight)

10 parts of C.P. Oelic Acid (by weight)

5 cc of "Degreased" Arabic Gum.

This method of forming the emulsion was always used:

Place in the agitator 18 parts of the oil and the 5 cc of arabic gum and agitate for 5 minutes or until thoroughly ground together.

The oelic acid was added and agitated until thoroughly mixed, then the remainder of the oil was added in three equal parts during the 10 minutes of agitation.

It was run through the homogenizer twice.

There was placed an equal amount of hot water in the agitator, and while agitating, the prepared oils were poured in small amounts during the process of agitation. The emulsion should be creamy white.

It was run through the homogenizer twice and agitated for five minutes.

### For Vegetable Oils

The following method proved to give greater stability when either cotton seed or cocoanut oil was substituted for the oelic acid. Either cocoanut oil or cotton seed oil was used for food products, while oelic acid would not be suitable on account of the taste as well as the toxicity effect.

The composition of the product to be emulsified was:

85 parts of oil

9 parts of cottonseed oil

10 cc of arabic gum

or

83 parts of oil

12 parts of cocoanut oil

10 cc of arabic gum

In container No. 1 was placed:

Cotton seed or cocoanut oil

5 cc of gum

In container No. 2 was placed:

Oil

5 cc of gum

Each container was agitated three minutes three different stirrings (intermittent stir-

ring). The contents of each container were poured into an equal volume of hot water under agitation, small amounts of one and then the other were added. Time of stirring, 10 minutes. It was homogenized twice, then stirred 5 minutes.

The gum solution was, for mineral oils, prepared in the following manner:

25 grams of finely arabic gum were weighed out, 10 cc of petroleum ether and 20 cc of benzene <sup>or ethyl alcohol.</sup> was added; agitated for five minutes. This formula could be made in any amounts provided the same proportions were used.

For Foods Products.

20 grams of powdered arabic gum was weighed out and was agitated five minutes with 30 cc of pure ethyl alcohol.

In both cases gum was always shaken before using and was added during the process of agitation.

Table I

|            |          |             |     |
|------------|----------|-------------|-----|
| Oil Phase  |          | Oil phase   | 70% |
| Oil        | 85 parts | Water phase | 30% |
| Oelie acid | 10 parts |             |     |
| Gum        | 5 parts  |             |     |

| <u>Oil</u>         | <u>Viscosity</u> | <u>Color</u> | <u>Stability</u> | <u>Remarks..</u>             |
|--------------------|------------------|--------------|------------------|------------------------------|
| Castor             | same             | white        | 2 days           | slight                       |
| Chinawood          | same             | white        | 2 days           | very slight at<br>separation |
| Cocoanut           | heavier          | white        | 8 weeks          | no separation                |
| Corn               | heavier          | white        | 4 weeks          | slight                       |
| Lemon grass        | same             | green        | 1 week           | slight                       |
| Lemon              | same             | white        | 1 week           | slight                       |
| Olive              | heavier          | white        | 8 weeks          | no separation                |
| Peanut             | same             | cream        | 8 weeks          | slight                       |
| Cottonseed         | heavier          | white        | 8 weeks          | no separation                |
| Peppermint         | same             | cream        | 8 weeks          | slight                       |
| Soy bean           | same             | white        | 8 weeks          | slight                       |
| Turpentine         | same             | white        | 4 weeks          | slight                       |
| Kerosene           | same             | white        | 6 weeks          | slight                       |
| Juniper            | same             | white        | 4 weeks          | slight                       |
| (Cheap)<br>Linseed | same             | yellow       | 3 weeks          | slight                       |
| Oelien             | same             | coffee       | 1 week           | partial separation           |
| Neetsfoot          | same             | cream        | 2 weeks          | slight                       |
| Paraffin           | same             | white        | 8 weeks          | very slight                  |

| <u>Oil</u>        | <u>Viscosity</u> | <u>Color</u> | <u>Stability</u> | <u>Remarks</u> |
|-------------------|------------------|--------------|------------------|----------------|
| Petrol            | same             | white        | 8 weeks          | very slight    |
| Petrolatum        | same             | white        | 8 weeks          | no separation  |
| Scale             | same             | cream        | 6 weeks          | very slight    |
| Verdol            | same             | cream        | 6 weeks          | very slight    |
| Sesame            | same             | white        | 1 week           | complete       |
| Sperm             | same             | white        | 1 week           | complete       |
| Stymax            | same             | white        | 3 weeks          | very slight    |
| Engine            | same             | yellow       | 3 weeks          | very slight    |
| Raw linseed       | same             | cream        | 3 weeks          | very slight    |
| Boiled<br>linseed | same             | cream        | 3 weeks          | none           |
| Linalool          | same             | white        | 36-48 hrs.       | complete       |
| Rape seed         | same             | cream        | 48 hrs.          | complete       |
| Turkey Red        | same             | brown        | 48 hrs.          | complete       |
| Creosote          | same             | red-brown    | 1 week           | slight         |
| Polarine          | same             | cream        | 3 weeks          | very slight    |
| Petroleum         | same             | white        | 3 weeks          | very slight    |
| Benz<br>aldehyde  | same             | white        | 3 weeks          | none           |
| Lanolin           | heavier          | cream        | 2 weeks          | none           |

Table II  
The Effect of Dilution

Oelie gum process

|                 | <u>Oil</u> | <u>H<sub>2</sub>O</u> | <u>Time of<br/>Stability</u> |               |
|-----------------|------------|-----------------------|------------------------------|---------------|
| Olive           | (90 parts  | 10 parts              | 8 weeks                      | no separation |
|                 | (66 parts  | 34 parts              | 8 weeks                      | no separation |
|                 | (33 parts  | 67 parts              | 8 weeks                      | no separation |
|                 | (5 parts   | 95 parts              | 7 weeks                      | very slight   |
| Scale<br>oil    | (90 parts  | 10 parts              | 6 weeks                      | no separation |
|                 | (66 parts  | 34 parts              | 6 weeks                      | no separation |
|                 | (33 parts  | 67 parts              | 5 weeks                      | very slight   |
|                 | (5 parts   | 95 parts              | 5 weeks                      | very slight   |
| Pepper-<br>mint | (90 parts  | 10 parts              | 8 weeks                      | slight        |
|                 | (66 parts  | 34 parts              | 8 weeks                      | slight        |
|                 | (33 parts  | 67 parts              | 8 weeks                      | no separation |
|                 | (5 parts   | 95 parts              | 8 weeks                      | no separation |
| Cocoanut        | (90 parts  | 10 parts              | 8 weeks                      | no separation |
|                 | (66 parts  | 34 parts              | 8 weeks                      | no separation |
|                 | (33 parts  | 67 parts              | 7 weeks                      | slight        |
|                 | (5 parts   | 95 parts              | 6 weeks                      | slight        |



Table III

|                |          |             |     |
|----------------|----------|-------------|-----|
| Oil            | 85 parts | Oil phase   | 70% |
| Cottonseed oil | 10 parts | Water phase | 30% |
| Arabic gum     | 5 parts  |             |     |

| <u>Oil</u> | <u>Viscosity</u> | <u>Color</u> | <u>Separation<br/>in</u> |                               |
|------------|------------------|--------------|--------------------------|-------------------------------|
| Corn       | heavier          | white        | 1 week                   |                               |
| Cocoanut   | heavier          | white        | 4 weeks                  |                               |
| Cottonseed | plastic          | white        |                          |                               |
| Olive      | heavier          | white        | 4 weeks                  |                               |
| Peanut     | heavier          | creamy       | 4 weeks                  |                               |
| Castor     | heavier          | creamy       | 24 hours                 | slight                        |
| Peppermint | heavier          | creamy       | 3 weeks                  |                               |
| Soy bean   | plastic          | creamy       | 3 weeks                  |                               |
| Paraffin   | same             | white        | 48 hours                 | slight                        |
| Sperm      | same             | white        | 10 hours                 | slight                        |
| Stymax     | same             | white        | 5 days                   | slight                        |
| Scale      | same             | tan          | 24 hours                 | complete                      |
| Verdol     | same             | creamy       | 10 hours                 | complete                      |
| Corn       | heavier          | white        | 8 days                   |                               |
| Castor     | heavier          | white        | 12-24 hrs.               |                               |
| Cottonseed | plastic          | white        | 3+ weeks                 | agitation<br>emulsified again |
| Olive      | heavier          | white        | 3 weeks                  | agitation<br>emulsified again |
| Peanut     | heavier          | creamy       | 3 weeks                  | agitation<br>emulsified again |
| Peppermint | heavier          | creamy       | 3 weeks                  | agitation<br>emulsified again |

| <u>Oil</u>       | <u>Viscosity</u> | <u>Color</u> | <u>Separation<br/>in</u> |                                      |
|------------------|------------------|--------------|--------------------------|--------------------------------------|
| Soy bean         | plastic          | creamy       | 3 weeks                  | agitation<br><u>emulsified</u> again |
| Paraffin         | same             | white        | 48-60 hours              |                                      |
| Sperm            | same             | white        | 24 hours                 |                                      |
| Stymax           | same             | white        | 6 days                   |                                      |
| Scale            | same             | tan          | 10 hours                 |                                      |
| Renown<br>Engine | same             | yellow       | 2 hours                  |                                      |

## Discussion

Colloidal theory indicates that in general any type of oily material, insoluble in water and that can be liquified under  $100^{\circ}\text{C}$  can be emulsified. In this work approximately thirty different oils were chosen at random and fair results were obtained. Castor, oelien, sesame, china wood had a life of about 48 hours while others remained free from separation for 8 to 10 weeks. In no case was the separation so marked that it could not be returned to the same creamy emulsion by a hand shaking of one or two minutes. Separation would not take place again for about 48 hours. These emulsions were heated to  $87^{\circ}\text{C}$  and dropped to  $-3^{\circ}\text{C}$  without any marked separation, that could not be removed by simply shaking by hand one or two minutes.

As previously stated, each oil is a special case and it is merely a problem of securing the correct ratio between the oelic acid, arabic gum and the oil to be emulsified. The same is probably true with the mineral oils with the use of either cotton seed or cocoanut oil as the emulsifier. The correct ratio between cotton seed oil and the oil to be emulsified was not determined. In the case

of the vegetable oils, the ratio was more nearly correct and the emulsions were far more stable.

The various other single emulsifiers used evidently required a second emulsifier for a successful emulsion. Glue, rosin, skimmed milk acting as a single emulsifier produced only one or two semi-permanent emulsions out of a group of thirty oils.

If a poorly made emulsion is allowed to stand, separation takes place almost immediately. An emulsion can be made using the correct ratio of oil and emulsifier, this same emulsion in a container containing a film of grease will break almost immediately. Bancroft (Applied Colloid Chemistry, Page 352) states "when free oil comes in contact with the film around the oil drops it tends to make it bend in the opposite direction, thereby cracking the emulsion." Grease in this case seemed to act the same way, that is, the grease destroyed the film, which in turn destroyed the emulsion.

All containers in this work were cleaned by boiling with dilute caustic soda and then rinsing with hot distilled water.

The method of diluting emulsions is important. The required amount of hot water should be added gradually to the emulsion under agitation. The

time of agitation should be about fifteen minutes; after the water has been added allow to agitate five minutes longer.

If gum is ground with alcohol the water will wet it immediately, while water alone fails to peptize it. Benzene, ether or any organic liquid with a low vaporization point can be substituted for the alcohol.

The action of the alcohol upon the gum is to remove the grease or foreign substances that encase the particles of gum.

### Summary

A permanent emulsion (48 hours or longer) could not be made by using inorganic metallic salts as emulsifiers.

Powdered iron, aluminum, magnesium were used as emulsifiers; a heavy plastic mass was formed which separated in a few hours.

Technique plays a very important part, especially intermittent stirring, also vessels free from grease are as important as the emulsifiers themselves.

Future experimental work with this method will be carried on in the following fields:

- (a) Acid Emulsions--such as nitro benzene with sulphuric acid.
- (b) Emulsions of waxes and semi-solids.
- (c) Pharmaceutical emulsions.
- (d) Soluble Oils.

DEC 21 '50

CHEMISTRY LIBRARY

MAY 23 '51

CHEMISTRY

T541

A648

94466

Applebee

MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 02446 7528