

THE RESISTANCE OF SPECIFIC FATTY ACIDS WHEN ADDED
TO CREAM TO NEUTRALIZATION BY SODIUM CARBONATE
AND CALCIUM HYDROXIDE

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AND CALCIUM HYDROXIDE

By

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INTRODUCTION

Through the deterioration of butterfat and the liberation of free fatty acids, certain objectionable flavors and odors are frequently produced in milk and other dairy products. It is almost universally agreed among workers in the field of dairy manufactures that rancidity and tallowiness are caused by fat deterioration. According to Rogers and associates (12), rancidity is due to the hydrolysis of fat and the liberation of the free fatty acids of lower molecular weights and tallowiness is due primarily to the oxidation of oleic acid. Fishiness is also closely associated with the decomposition of fat. Work cited by Rogers (12) has established the fact quite conclusively that fishiness is caused by the hydrolysis of lecithin resulting in the production of trimethylamine which is responsible for the fishy flavor.

Butterfat contains a relatively high percentage of the fatty acids of lower molecular weights and since water is always present in appreciable amounts in most all forms of dairy products, the susceptibility to hydrolysis is very great. Data obtained by Holland et al (10) in the analysis of several samples of butter showed that oleic acid comprised from 25.273 to 40.313 per cent (average 31.895 per cent) of the fatty acids of butterfat. A high percentage of low molecular weight fatty acids in the presence of water and a high percentage of oleic acid make butterfat more susceptible to deterioration than most all other fats.

The action of enzymes and free acids in the presence of water and the action of certain microorganisms are responsible for the liberation of free fatty acids. The lipases are the enzymes that have the property of hydrolyzing butterfat. Pasteurization renders this group of enzymes partially, if not totally inactive. Since the majority of the fluid milk

is pasteurized and marketed before appreciable amounts of acid have had time to develop, little difficulty with rancidity is encountered in this product.

The situation in the butter industry is somewhat different. The bulk of the cream which is used for butter production usually attains an age of several days before it is marketed. During this time, it is kept in the raw state, and in most cases, at temperatures favorable for rapid bacterial growth. Extreme conditions of this type are found in the Southwest during the warmer months. Titratable acidities ranging from 0.75 to 1.25 per cent are common. Recent surveys in which the author assisted show that cream in this immediate section of Oklahoma not only had high titratable acidities, but also, in many cases, high fat acidities.

A relatively large amount of literature has been published on the neutralization of the titratable acidity of cream for butter making, but a comparatively small amount of material is available which deals specifically with the neutralization of the free fatty acids of cream. In view of this fact, some work has been done at this institution to determine the effectiveness of various commercial neutralizers upon the neutralization of free fatty acids of cream having high fat acidities due to the action of lipolytic microorganisms. Wide variations were encountered between the effectiveness of these neutralizers upon the neutralization of the fat acidity. In working ^{with} the relation of volatile acidity of butterfat to rancidity, Fouts (7) found that the different organisms studied varied considerably in the percentages of total fat acids that were volatile and non-volatile. In view of these facts, the belief was advanced that some of the individual fatty acids were more

resistant to neutralization than others, and also, that the resistance offered by these acids perhaps varied with the different neutralizers. It was this belief that led the author to undertake the problem presented here.

Since the time allotted for this study was limited, only two neutralizers were studied with regards to their effectiveness upon the nine more important fatty acids of butterfat. Chemically pure calcium hydroxide and sodium carbonate were used in these experiments. It is believed that since these two neutralizers are representative of the two types of neutralizers used commercially that a rather accurate picture of the general effectiveness of neutralization upon the various fatty acids is presented.

HISTORICAL

It has been known for several years that the acidity of butter greatly affects its keeping quality. Salted butter with a high acidity often develops a fishy flavor within a short time under commercial storage conditions. Hunziker (11) reported the development of a fishy flavor in a sample of butter after fifteen days of storage.

Several investigations have been conducted for the purpose of determining the effect of the neutralization of cream upon the acidity of the resulting butter. Hunziker (11) was perhaps among the first to attempt such a study. He reported that when the acidity of a sample of cream was reduced from 0.70 to 0.24 per cent, the acidity of the butter was reduced from 0.150 to 0.119 per cent (calculated as lactic acid). When a portion of this neutralized cream was pasteurized at 145° F. for 30 minutes the acidity was further reduced to 0.19 per cent and the acidity of the butter was reduced to 0.060 per cent. At the end of a seven-month storage period a sample of butter from the raw portion of this cream had a fishy flavor and scored 84. The butter from the cream that was neutralized only, had a slight rancid flavor and scored 89, while a sample of butter from a portion of the cream that was neutralized and pasteurized had a clean flavor and scored 90 at the end of the seven-month period.

More recent investigations of this kind were conducted by Gould and Townley (9). They investigated the influence of various neutralizers upon the acidity of butter and butterfat. The data obtained from this experiment show that the acidity of butter and butterfat decreases with successive reductions in the acidity of cream. These data also show a wide variation in the effectiveness of the neutralizers in reducing the

acidity of butter and butterfat. They (9) state that:

"In general, the limes were less efficient in reducing the acidity of the butter than were the other neutralizers, at least throughout the calculated range of 0.25 to 0.05 per cent."

In working with the correlation between the pH of the cream and the pH of the resulting butter, Breazeale et al (4) obtained more favorable results with soda neutralizers than they did with lime neutralizers. When the pH of the butter was plotted against the pH of the neutralized cream from which it was churned, smoother curves were obtained in the trials with soda than in the trials with lime neutralizers. The pH of the butter from the cream that was neutralized by the lime took a sudden rise from 6.25 to 7.0 while the pH of the cream varied only from 6.3 to 6.6. When a portion of the same cream was neutralized with a soda, a smooth curve was obtained throughout the range of 5.5 to 8.0.

In working with samples of cream with relatively high fat acidities, Fouts (6) obtained data which agree very favorably with that of Gould and Townley (9) with regards to the effectiveness of neutralization of cream upon the acidity of butterfat. The titratable acidity of these samples ranged from 0.47 to 0.82 per cent and the fat acidities ranged from 1.2 to 5.9. After neutralization, the acidity of the cream ranged from 0.23 to 0.27 per cent and the fat acidities of the resulting butter were decreased to a range of 1.0 to 1.5. In another phase of this experiment he also found that sodium carbonate was more effective than magnesium oxide in reducing fat acidities at points of neutralization of the cream above 0.10 per cent. At the end point, magnesium oxide was more effective. The data of Gould and Townley (9) show that caustic soda was the only alkali used that was more effective than magnesium oxide in reducing fat acidities at this point. The results of further investigations made by

Fouts et al (8) show that progressive neutralization of cream reduced the acidity of the resulting butterfat, but that this decrease was not directly proportional to the per cent decrease in the acidity of the cream. When high acid cream was neutralized, the reduction of the acidity of the fat was very slight until an appreciable amount of the acidity of the cream was neutralized. Bird (2) stated that there is some correlation between the reduction of the acidity of cream and the acidity of fat. As the acidity of cream is reduced, the acidity of the fat is likewise reduced.

The results of the work of Bendixen (1) indicate that there was a direct relationship between the ratio of the acidity of the butterfat to the acidity of the butter and the flavor score of butter. As this ratio $\left(\frac{\text{acid value of fat}}{\text{acid value of butter}} \times 100\right)$ increased the flavor score decreased. Both, the ratio and the flavor criticisms, indicate that there was fat deterioration.

STATEMENT OF PROBLEM

This problem was undertaken for the purpose of obtaining information regarding the resistance of the nine more common fatty acids of butterfat, when added separately to cream, to neutralization by calcium hydroxide or sodium carbonate.

STRATHMORE PARCHMENT

100% RAG U.S.A.

PLAN OF PROCEDURE

Preliminary Phase

Before attempting this problem, it was necessary to find some means by which the various fatty acids might be added to the cream most successfully. It was desired to keep the condition of the cream as near its natural state as possible, and yet, obtain a thorough distribution of the fatty acids. Several methods were tried but only the one which proved most successful will be described here.

Fresh sweet cream of good quality was standardized to 33 per cent fat and pasteurized at 145° F. for 30 minutes. It was then cooled to 70° F., inoculated with lactic acid ferment culture and incubated at room temperature until the titratable acidity had reached approximately 0.80 per cent. Formaldehyde was then added at the rate of one part formaldehyde gas to 2,000 parts of cream so that further action of microorganisms would be reduced to a minimum.

The cream was then divided into 10 portions of 75 gm. each. One portion was used for each of the nine fatty acids studied and one was carried through as a blank determination. A definite amount of each of the fatty acids was added to the sample of cream provided for it. The acids were first added to portions of filtered, low acidity butterfat equal in weight to 10 per cent that of the sample of cream to which it was added. In this case 7.5 gm. of fat was used. Twice this amount (15.0 ml.) of distilled water was added so that the mixture would be 33 per cent fat. Before mixing, the portions of fat containing the fatty acids, the distilled water and the cream were brought to 175° F. in a water bath. This temperature was used because it is well above the melting point of stearic acid which is the acid of the group having the

highest melting point. Immediately after mixing the water, fat and cream, the mixture was run through a small hand emulsifier. The samples were then incubated at 113° F. for 18 hours. At this temperature the butterfat was in a liquid state and it seemed that a thorough distribution of the fatty acids was obtained.

At the end of the 18-hour incubation period, the titratable acidity of each sample of cream was determined. The samples were then cooled and churned, after which, the acidities of the buttermilk and fat were determined. The fat was prepared for the determination of its acidity by first, melting the butter in an incubator at 113° F. and then aspirating off the fat into filtering apparatus. Filtration was also carried out in the incubator at 113° F.

The data obtained in the preliminary phase are given in table I. These data were used for calculating the amount of each fatty acid to be added to the cream of its respective series. After ripening, the percent acidity of the cream was 0.84 and the acidity of the fat was 0.7.

Table I shows that the calculations for lauric acid were a little high. This was adjusted before the major part of these experiments was begun. The amount of butyric acid added and the effect it had upon the acidity of the cream are significant as will be shown later.

Table I

Results of a Trial to Determine the Amounts of the
Various Fatty Acids Needed to Yield the
Desired Fat Acidity

(The fat acidity calculated for each sample was 6.0)

Sample No.	Fatty acid	Grams acid added	Acidity of cream	Fat acidity
1	:blank	: 0.000	: 0.85	: 0.9
2	:butyric	: 0.813	: 1.35	: 7.3
3	:caproic	: 0.300	: 0.89	: 8.0
4	:caprylic	: 0.308	: 0.85	: 8.2
5	:capric	: 0.360	: 0.85	: 7.9
6	:lauric	: 0.568	: 0.83	: 10.3
7	:myristic	: 0.456	: 0.83	: 7.6
8	:palmitic	: 0.513	: 0.84	: 7.2
9	:stearic	: 0.534	: 0.84	: 7.6
10	:oleic	: 0.654	: 0.83	: 7.9

Experimental Phase

The cream used in the experimental phase of this problem was of the same quality as that of the preliminary phase and was treated in the same manner. Since only one fatty acid was dealt with at a time, no divisions of the cream were made before the addition of this acid. The calculated amount of the desired fatty acid was added to 2,400 gm. samples of cream in the same manner as described under the preliminary phase.

At the end of the 18-hour incubation period, the mixture was divided into 24 one-hundred-gm. samples. Eleven of these samples were neutralized progressively with calcium hydroxide while 11 others were neutralized in the same manner with sodium carbonate. The two remaining samples were taken through the process as blank determinations. The calculated points of neutralization were 0.75, 0.50, 0.40, 0.35, 0.30, 0.25, 0.20, 0.15, 0.10, 0.05, and 0.00 per cent. All neutralizations were carried out at 90° F. and the samples were held at this temperature

for 15 minutes before pasteurization. The lime neutralizer used was a $12\frac{1}{2}$ per cent calcium hydroxide and water mixture; the soda, a 10 per cent solution of sodium carbonate. These are the strengths of the two neutralizers commonly recommended for commercial practices. The samples were pasteurized at 145° F. for 30 minutes.

During neutralization and pasteurization, all samples were held in the same water bath. The bath was equipped with 12 small agitators of the same design. They were driven by the same force; a $1/50$ H. P. variable speed electric motor. Some idea of this machine may be obtained by referring to figure 1 which is an actual photograph of it. Figure 2 is a close up view of one of the small agitators. This machine proved to be very efficient in this type of work. It was designed by members of the staff and the author.

After neutralization, titratable acidities of each sample were determined. They were then cooled and churned. The churning was done on a small experimental churn which was designed for holding twelve 8 oz. jars. Figure 3 is an actual photograph of this churn. It consists of the base of a treadle type sewing machine in an inverted position. The frame for holding the jars in position is mounted on the treadle. It is driven by a small variable speed electric motor. This machine was also designed by a member of the staff.

Duplicate runs were made on the butyric, caproic, caprylic, lauric, palmitic, and oleic series. The results obtained in the duplicate series in each case checked very favorably with the results of the original series. Since good checks were obtained in those series on which duplicate determinations were made, and since a comparatively large number of samples were run in each series, duplicate determinations on all series

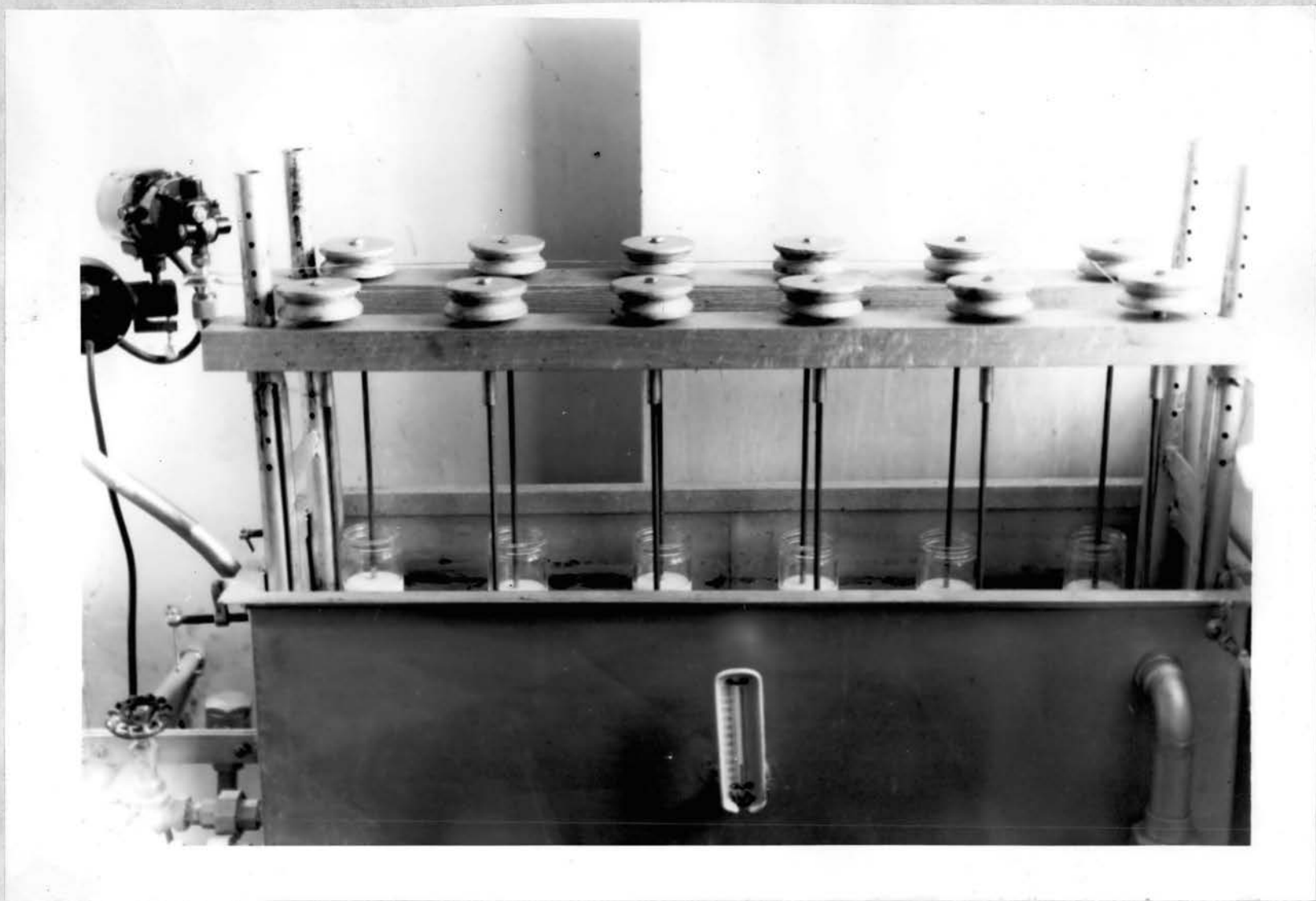


Figure 1

Water Bath and Multiple-agitators for Handling 12 Samples

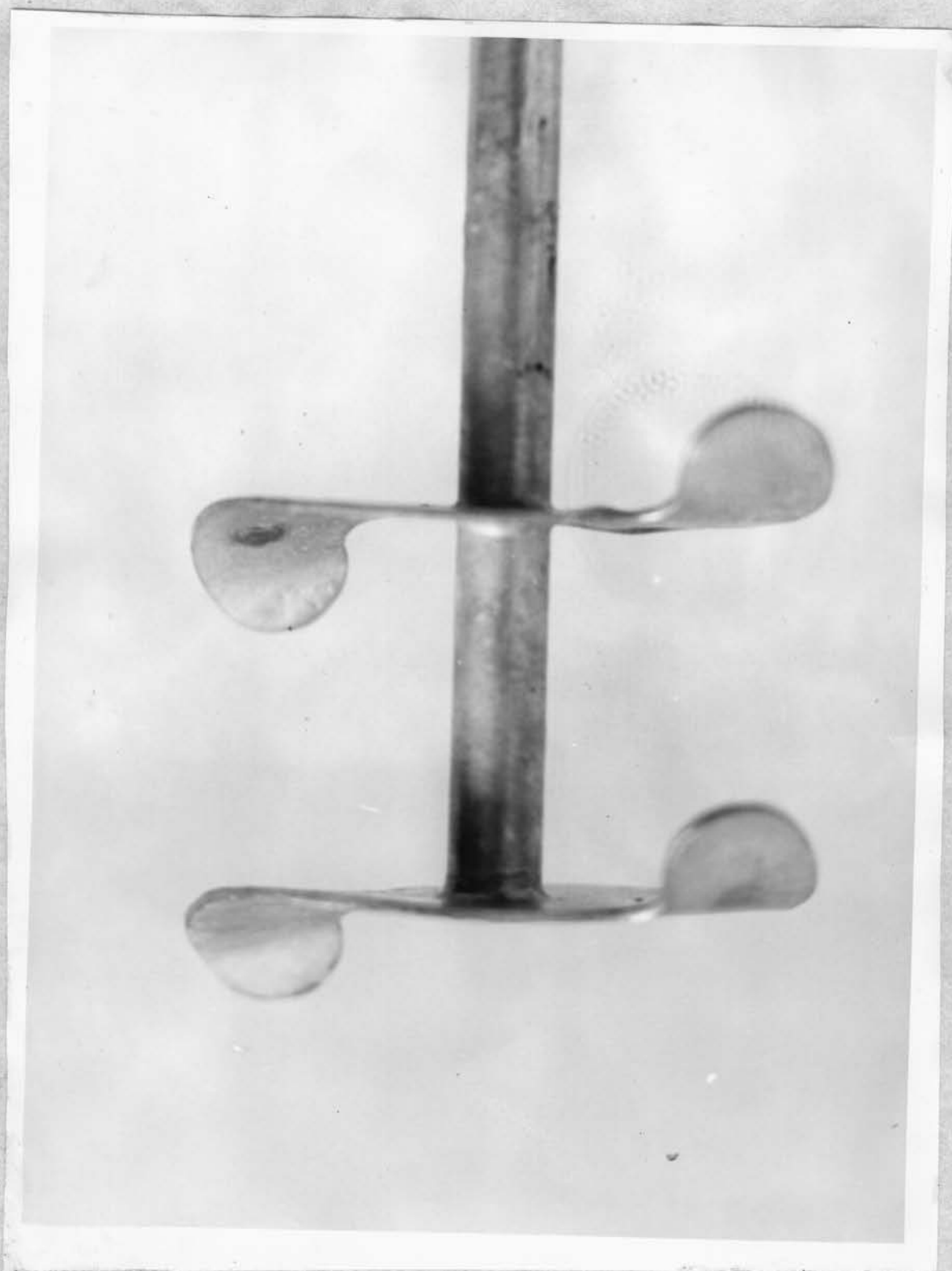


Figure 2

Closeup of One of the Agitators Shown in Figure 1

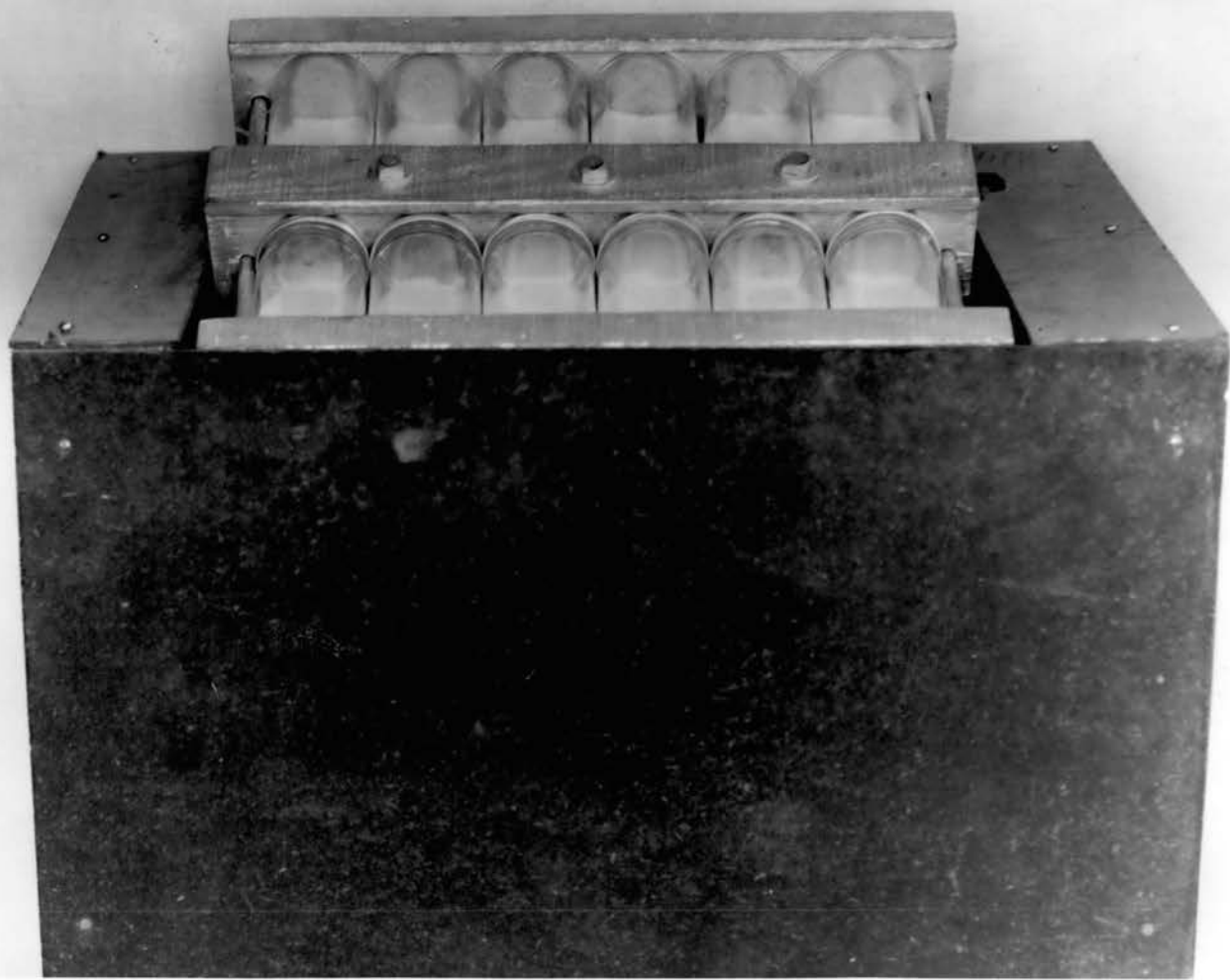


Figure 3

Small Experimental Machine for Churning Several Samples
at the Same Time

were not made. Furthermore, all acids on which duplicate runs were not made reacted in the original runs very similar to one or more of the acids on which a duplicate run was made.

Another phase of this problem consisted of an experiment in which a mixture of the nine fatty acids considered in this problem was used. The amount of each fatty acid to use was calculated from data cited by Rogers (12). Since these nine fatty acids do not comprise all the fatty acids of butterfat, the sum of their percentages does not total exactly 100 per cent. When converted to a 100-per-cent basis, the following percentage for each acid was obtained:

Butyric	3.2 per cent
Caproic	2.1 per cent
Caprylic	0.8 per cent
Capric	1.7 per cent
Lauric	6.2 per cent
Myristic	20.2 per cent
Palmitic	15.3 per cent
Stearic	15.5 per cent
Oleic	34.5 per cent

The fatty acids were weighed out and heated together until all the crystals were melted. Fifteen ml. of this mixture was then transferred by means of a hot pipette to low acid butterfat equal in weight to 10 per cent that of the sample of cream to which it was to be added. The fat containing the mixture of acids was added to the cream in the same manner as has already been described for adding the fatty acids to the cream samples.

Determinations

The following determinations were made on all samples of each series:

1. Original acidity of the cream.
2. Acidity of the cream after ripening.
3. Fat acidity of original cream.
4. Fat acidity after ripening.
5. Fat acidity after addition of fatty acid.
6. Acidity of cream after neutralization and pasteurization.
7. Acidity of buttermilk.
8. Fat acidity after neutralization and pasteurization.

Observations were made throughout the entire procedure and all irregularities such as oiling off, difficult churning and other unnatural characteristics were noted. Comparisons of the flavor and odor were made between samples of butter of the same series at various stages of neutralization with the same neutralizer. Samples of the same series that were neutralized with soda were compared with those that were neutralized with lime. The fat acidities were determined by a slight modification of the Alcoholic Potassium Hydroxide Method (A) of Bird and Breazeale (3). Ten gm. of fat were weighed into 125 ml. Erlenmeyer flasks. Twenty-five ml. of petroleum ether, 10 ml. of absolute alcohol and 10 drops of alcoholic phenolphthalein were added and the titrations were made with N/10 potassium hydroxide in absolute alcohol. The first definite color change was taken as the end point.

Fat acidity is expressed as the number of milliliters of normal potassium hydroxide required to neutralize the free fatty acids of 100 gm. of filtered fat using phenolphthalein as an indicator. This meaning

will be implied when the term fat acidity is used throughout this thesis.

DISCUSSION OF RESULTS

The aim of this thesis is to present data showing the resistance offered to neutralization by individual fatty acids when added singly to cream. Two neutralizers, calcium hydroxide and sodium carbonate, were considered.

Before a discussion of the resistance of the individual fatty acids to neutralization and the effectiveness of the two neutralizers in the reduction of these acids is in order, a brief review should be made of some of the physical characteristics of this group of fatty acids.

Table II which is a modification of the data presented by Rogers (12), gives some of the more important physical characteristics of these acids. It will be noted that butyric acid is completely soluble in water and that caproic acid is soluble to the extent of 0.882 gm. per 100 ml. of water at 59° F. At 212° F., the solubility of caprylic acid is 0.25 gm. and capric is 0.10 gm. per 100 ml. of water. Lauric acid is very slightly soluble and the remaining acids are insoluble in water.

Table II

Some Physical Constants of the Nine More Common Fatty Acids of Butterfat

Acid	: Melting point	: Boiling point	: Solubility in 100 ml. water
Butyric	: 20.0° F.	: 325.5° F.	: soluble
Caproic	: 17.6° F.	: 395.6° F.	: 0.882 gm. at 59° F.
Caprylic	: 61.7° F.	: 456.8° F.	: 0.25 gm. at 212° F.
Capric	: 88.3° F.	: 514.4° F.	: 0.10 gm. at 212° F.
Lauric	: 110.5° F.	: 572.0° F.	: very sl. soluble
Myristic	: 129.2° F.	: -----	: insoluble
Palmitic	: 145.4° F.	: -----	: insoluble
Stearic	: 156.7° F.	: -----	: insoluble
Oleic	: 60.8° F.	: -----	: insoluble

Large amounts of butyric acid were required to increase the acidity of the fat in the butyric series to a point comparable to the points used in the other series. Table III shows that the addition of 23.0 ml. of butyric acid to 2,400 gm. of cream increased the acidity from 0.70 to 1.35 per cent while the acidity of the fat was increased from 1.0 to 5.7. This table also shows that caproic acid increased the acidity of the cream from 0.82 to 0.85 and that all the acids of higher molecular weights had little influence upon the acidity of the cream. The mixture of fatty acids slightly increased the acidity of the cream to which it was added.

Table III

Results of Adding Definite Amounts of Fatty Acids
to 2,400-Gram Samples of Cream

Acid added	Amount	Acidity of cream		Acidity of fat	
		Before	After	Before	After
Butyric	23.0 ml.	0.70	1.35	1.0	5.7
Caproic	10.0 ml.	0.82	0.85	0.8	6.6
Caprylic	9.0 ml.	0.90	0.89	0.8	8.0
Capric	10.0 ml.	0.85	0.85	0.7	7.0
Lauric	11.0 gm.	0.80	0.80	0.7	7.0
Myristic	12.0 gm.	0.82	0.82	0.7	7.5
Palmitic	17.0 gm.	0.89	0.90	0.6	7.4
Stearic	14.0 gm.	0.90	0.90	0.7	6.4
Oleic	19.0 ml.	0.80	0.80	1.0	6.2
Mixture	15.0 ml.	0.83	0.85	0.6	6.3

Data obtained by Ferg (5) show that when butyric acid was added to cream at the rate of 0.5 ml. to 100 gm. of cream, approximately 80.0 per cent of the acid went to the water phase and approximately 20.0 per cent went to the fat phase. This is, no doubt, due to a close physical relationship between this acid and water. His data denote that the affinity of butyric acid for water is about four times as great as it is for fat. In working with caproic acid, Ferg (5) found that when 0.5 ml. of the acid was added to 100 gm. of cream 77.4 per cent went to

the fat phase and 22.6 per cent went to the water phase. He also found that approximately 96.0 per cent of caprylic and capric acids went to the fat phase. All of the remaining fatty acids used in these experiments were found to go completely to the fat phase.

An analysis of the data obtained from the experiments of this problem revealed that certain of the fatty acids reacted to neutralization in a very similar manner. Since this was found to be true, the acids were divided into three groups so as to simplify the discussion of the results. These groups are as follows:

Group I - butyric and caproic.

Group II - caprylic, capric, lauric, myristic, palmitic and stearic.

Group III - oleic.

Comparative Resistance of the Fatty Acids

The data herein presented show that the resistance offered to neutralization by both the fatty acids of Group I was slight. Figures 4 and 6 and table IV show that caproic acid was a little more resistant than butyric.

Figures 5 and 7 and table V should not be considered in a comparison of the resistance of butyric acid because the acidity of the cream of this series was about twice that of the other series. These two figures are intended to show the comparative resistance to the various fatty acids to different fractional parts of equivalent weights of the neutralizers. Since the titratable acidity of the cream of the butyric series was about twice that of the other series studied a much greater amount of neutralizer was required to reduce this excess acid. Thus, it was impossible to compare the resistance of butyric acid with the other acids with regards to the amount of neutralizer required.

Table IV

Per Cent of Fatty Acids Neutralized at Various Points
of Neutralization of Cream

Fatty acids	Original		Alkali	Points of neutralization of cream						
	acidity Cream	Fat		0.50	0.35	0.25	0.20	0.15	0.10	0.05
Butyric	1.35	5.3	Ca(OH) ₂	53.2	67.3	71.4	79.7	80.5	84.2	89.9
			Na ₂ CO ₃	61.4	72.0	80.5	83.1	87.2	88.6	91.2
Caproic	0.85	6.6	Ca(OH) ₂	42.5	66.6	72.7	75.8	80.3	87.9	95.5
			Na ₂ CO ₃	40.5	71.2	81.8	86.2	89.4	93.5	93.5
Caprylic	0.90	8.0	Ca(OH) ₂	12.5	21.2	47.6	58.6	78.1	85.4	93.6
			Na ₂ CO ₃	12.5	34.1	47.4	63.3	81.8	88.3	91.0
Capric	0.85	7.0	Ca(OH) ₂	22.9	9.7	24.3	34.3	64.3	78.2	91.5
			Na ₂ CO ₃	7.9	28.6	47.2	64.3	81.5	91.5	92.9
Lauric	0.80	7.0	Ca(OH) ₂	2.6	19.5	44.0	59.5	77.5	83.2	90.1
			Na ₂ CO ₃	8.2	26.6	59.1	70.5	81.3	86.5	90.0
Myristic	0.82	7.5	Ca(OH) ₂	4.0	12.0	38.7	61.3	77.3	86.7	94.7
			Na ₂ CO ₃	9.3	21.3	40.0	57.3	77.3	86.7	89.2
Palmitic	0.89	7.4	Ca(OH) ₂	8.3	28.1	46.8	62.6	78.0	83.5	91.6
			Na ₂ CO ₃	9.8	32.1	66.8	80.0	87.5	91.4	92.1
Stearic	0.90	6.4	Ca(OH) ₂	7.8	19.8	37.5	42.2	75.0	87.5	92.2
			Na ₂ CO ₃	7.8	21.9	39.1	59.1	79.4	87.5	91.0
Oleic	0.80	6.2	Ca(OH) ₂	2.3	6.1	16.2	30.1	52.5	65.5	85.9
			Na ₂ CO ₃	2.2	5.4	17.8	28.9	48.2	62.5	70.8
Mixture	0.85	6.3	Ca(OH) ₂	6.8	8.3	27.8	36.4	52.5	61.8	79.2
			Na ₂ CO ₃	7.1	11.9	48.3	52.0	61.9	76.1	82.4

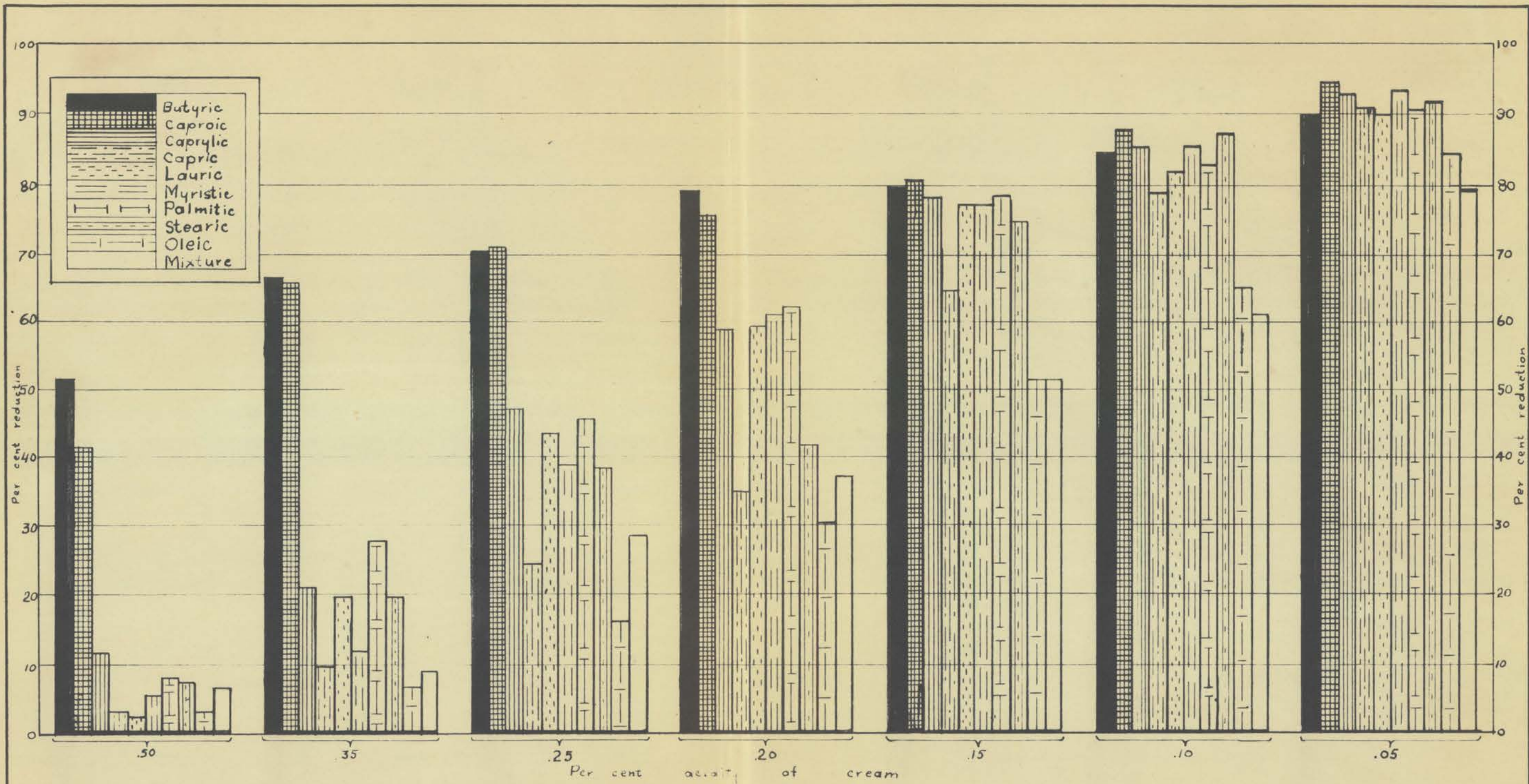


Fig. 4.— Per Cent Reduction of Fat Acidity in Cream Containing Known Added Fatty Acids When the Titratable Acidity Was Decreased by the Addition of Calcium Hydroxide

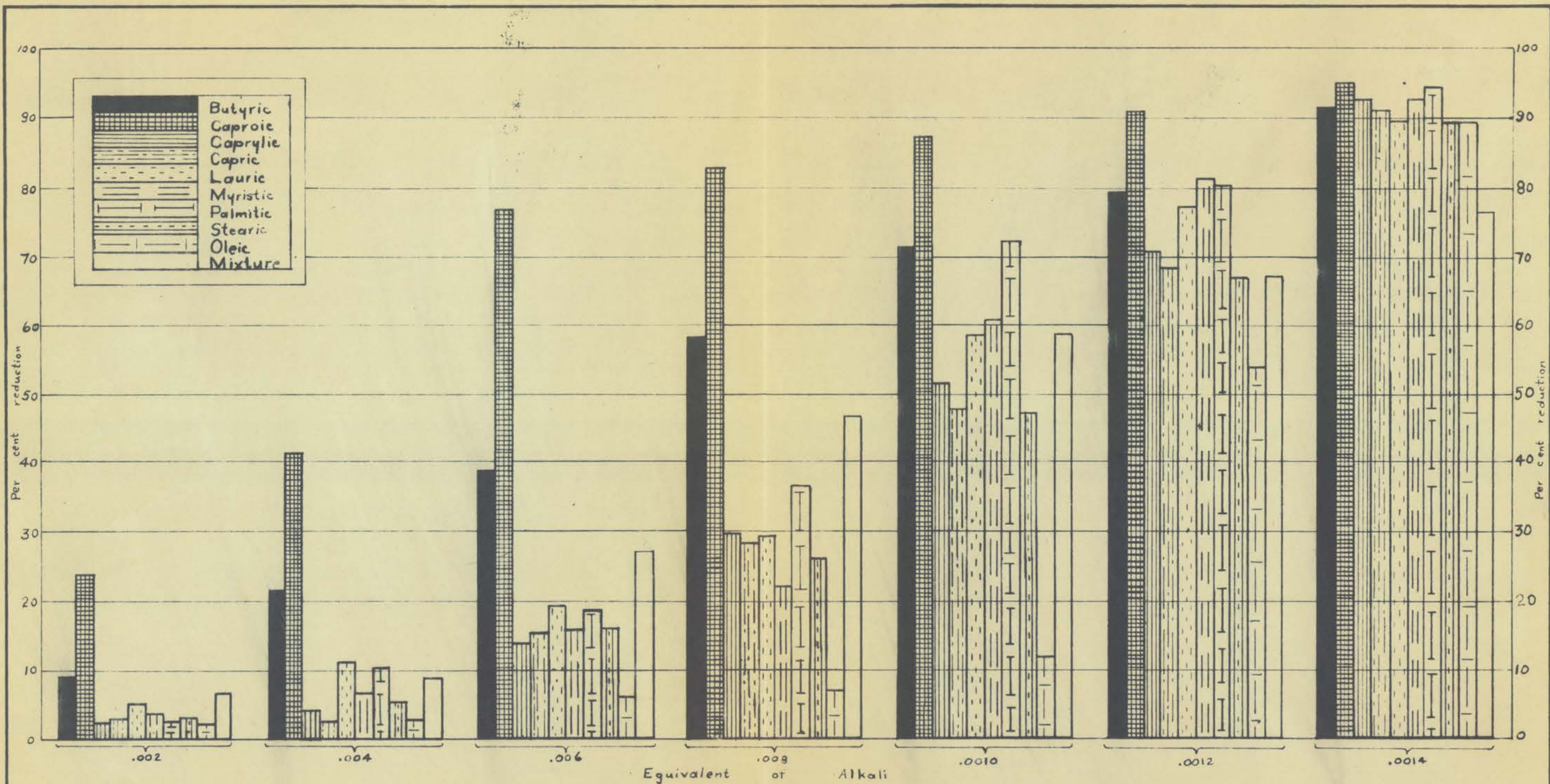


Fig. 5.— Per Cent Reduction of Fat Acidity When Fractional Parts of Equivalent Weights of Calcium Hydroxide Were Added to 100 Grams of Cream Containing Known Added Fatty Acids

Table V

Per Cent of Fatty Acids Neutralized by Equivalent Weights of Alkali When Added to 100 gm. Cream

Fatty acids	Original acidity		Alkali	Equivalent weights of alkali						
	Cream	Fat		0.002	0.004	0.006	0.008	0.010	0.012	0.014
				Per cent of fatty acids neutralized						
Butyric	1.35	5.3	Ca(OH) ₂	9.1	22.4	38.5	57.9	72.0	79.4	92.1
			Na ₂ CO ₃	11.8	24.9	37.5	55.0	75.4	87.0	90.0
Caproic	0.85	6.6	Ca(OH) ₂	24.4	41.6	76.5	82.8	87.4	91.3	95.0
			Na ₂ CO ₃	21.5	50.7	80.0	86.3	90.0	92.1	92.7
Caprylic	0.90	8.0	Ca(OH) ₂	2.9	4.1	13.0	29.3	52.3	71.6	93.6
			Na ₂ CO ₃	2.5	13.6	27.5	46.8	58.0	70.0	87.3
Capric	0.85	7.0	Ca(OH) ₂	3.1	3.4	15.6	28.2	47.6	68.7	91.5
			Na ₂ CO ₃	4.1	11.0	30.7	50.3	80.0	85.2	91.0
Lauric	0.80	7.0	Ca(OH) ₂	5.1	11.4	19.2	29.1	57.8	76.8	89.2
			Na ₂ CO ₃	10.0	20.0	32.1	47.6	70.3	84.0	89.6
Myristic	0.82	7.5	Ca(OH) ₂	3.9	6.7	16.2	22.5	61.0	81.7	94.7
			Na ₂ CO ₃	5.0	18.1	40.0	67.2	81.5	87.0	89.6
Palmitic	0.89	7.4	Ca(OH) ₂	3.1	10.1	17.9	35.6	72.3	81.0	94.9
			Na ₂ CO ₃	11.5	26.5	57.4	75.0	82.4	88.2	92.0
Stearic	0.90	6.4	Ca(OH) ₂	3.4	5.3	16.4	26.2	47.2	66.3	89.1
			Na ₂ CO ₃	7.0	16.1	27.5	62.0	77.2	88.6	90.0
Oleic	0.80	6.2	Ca(OH) ₂	2.3	3.0	5.6	7.1	12.2	54.0	88.9
			Na ₂ CO ₃	1.9	5.1	22.0	42.0	51.8	57.9	70.0
Mixture	0.85	6.3	Ca(OH) ₂	6.0	8.7	26.8	46.5	58.3	66.9	75.8
			Na ₂ CO ₃	2.1	5.0	9.0	49.0	56.3	67.0	78.2

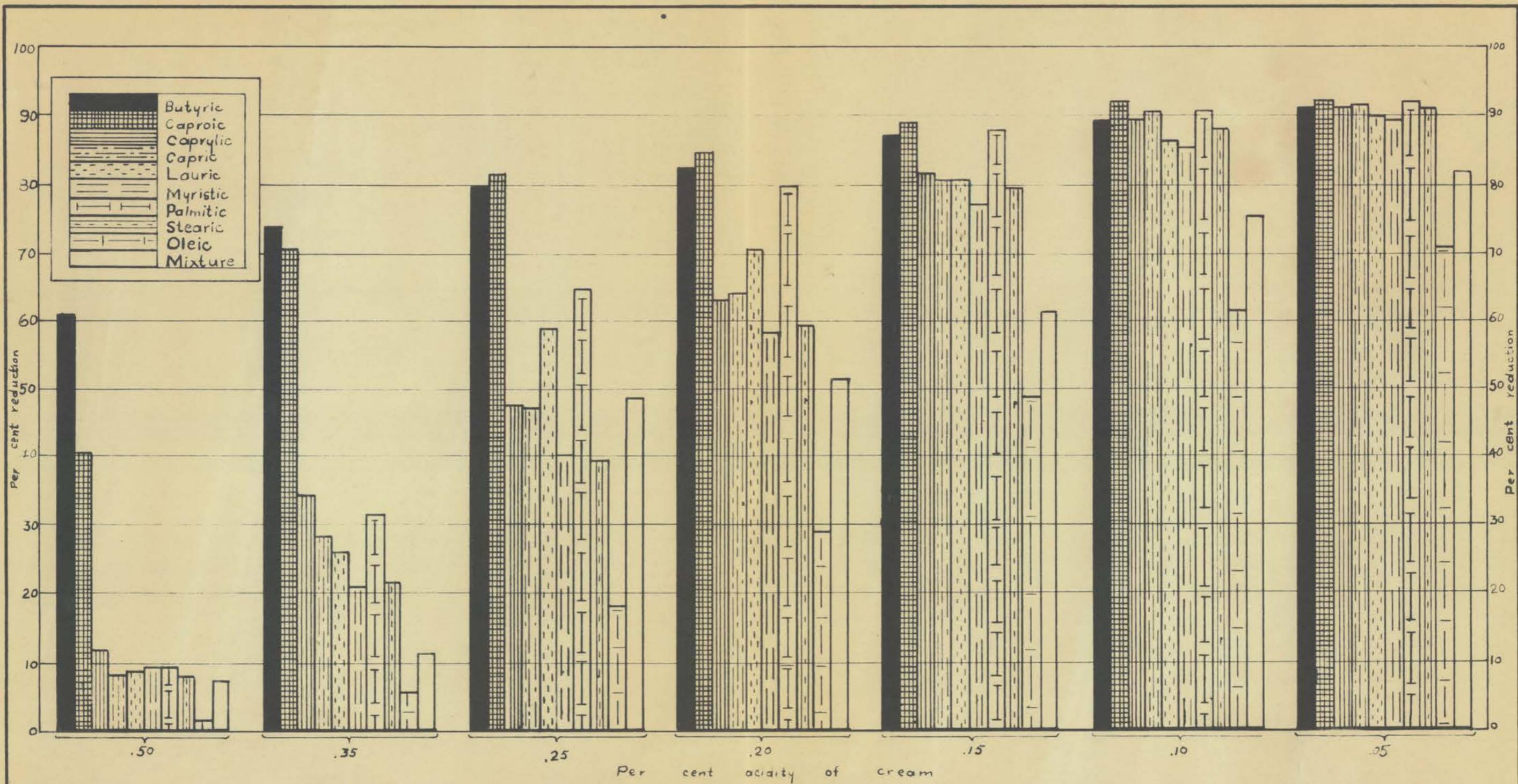


Fig. 6.— Per Cent Reduction of Fat Acidity in Cream Containing Known Added Fatty Acids When the Titratable Acidity Was Decreased by the Addition of Sodium Carbonate

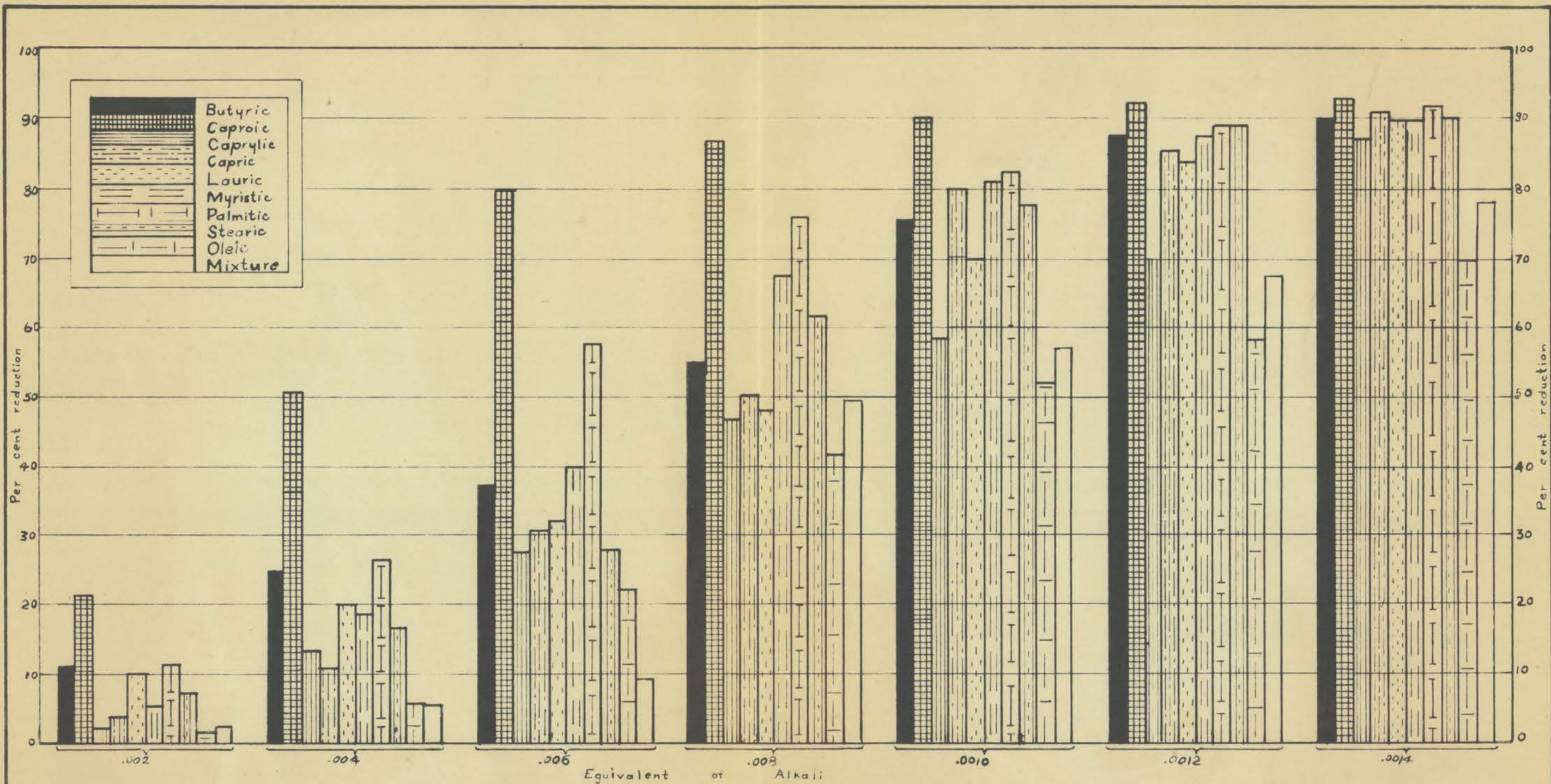


Fig. 7.— Per Cent Reduction of Fat Acidity When Fractional Parts of Equivalent Weights of Sodium Carbonate Were Added to 100 Grams of Cream Containing Known Added Fatty Acids

The high acidity of the butyric series was due to the greater affinity of butyric acid for water than for butterfat. Large amounts of this acid had to be added to the cream of the butyric series in order to increase the fat acidity to a point comparable to the points used in the other series. To overcome this condition, the author considered the possibility of adding butyric acid to low acid cream, but in so doing, the cream would not have been given the same treatment as it was in the other series. It was then, decided to treat all samples as near the same as possible.

When the fat acidities of the butyric and caproic series were plotted against the acidity of the cream at the various points of neutralization, straight diagonal lines were obtained until low acidities were reached. Figure 8 which was plotted from the data of the caproic series is a representative curve of the acids of group I. This figure also shows that the resistance offered by the acids of this group was very slight.

The acids of group II resisted neutralization much more than the acids of group I. This resistance varied somewhat between the acids, but this variation did not follow any set rule. In all series, little reduction of these acids took place until low titratable acidities of the cream were reached. At 0.25 per cent acidity of the cream, only two of these acids were reduced as much as 50.0 per cent. In general, at 0.15 per cent acidity of the cream, 80.0 per cent of most of these acids was reduced. This is significant because 0.15 to 0.25 per cent acidity is usually considered the normal range of neutralization of cream for butter making. Table IV and figures 4 and 6 show that the most rapid reduction of the acids of group II occurred from 0.35 down to 0.15 per

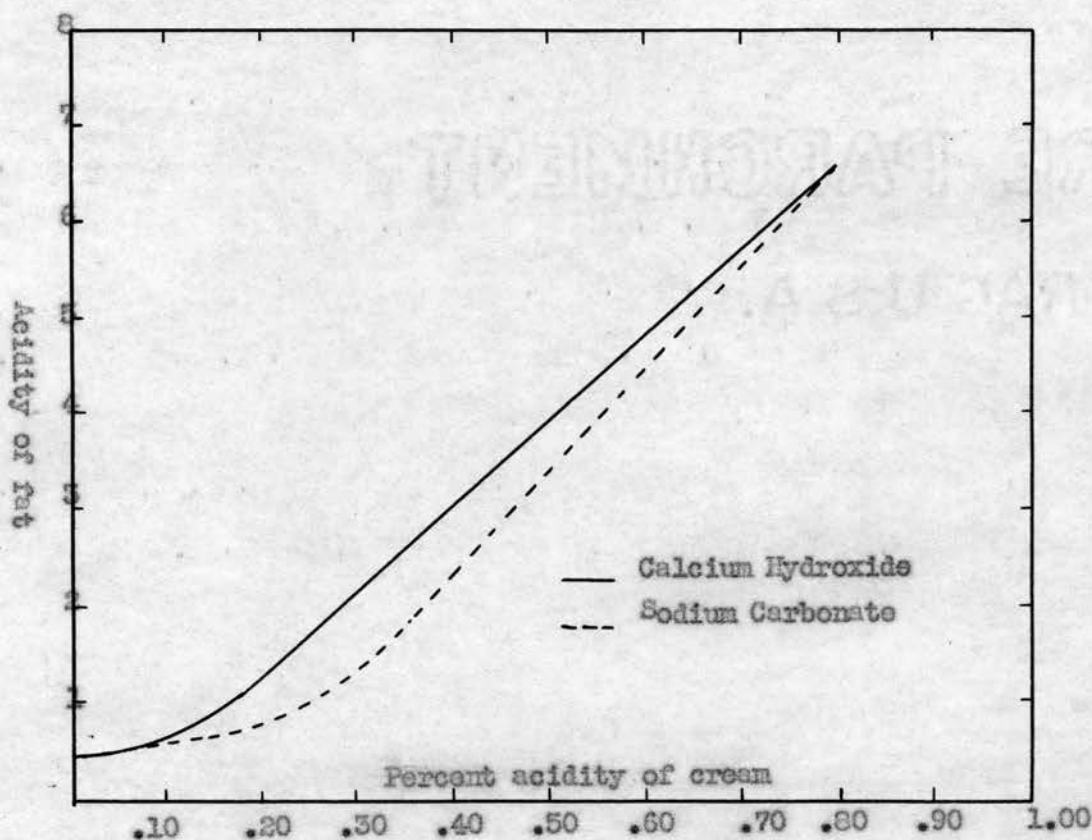


Figure 8. Effect of Neutralization of Cream with Calcium Hydroxide and Sodium Carbonate Upon Fat Acidity Which Was Increased by Addition of Caproic Acid.

cent acidity of the cream. Figure 9 was plotted from the data obtained in palmitic series, but it is representative of the type of curve that all the acids of Group II present. It will be noted that a sudden drop in the curve takes place at approximately 0.35 percent acidity of the cream and continues to drop rapidly until approximately 0.15 per cent acidity of the cream is reached. Roughly 70.0 per cent of these acids are reduced within this 0.10 per cent drop in the acidity of the cream.

Oleic acid offered the greatest resistance of all the acids used in these experiments. It will be noted from Figure 10 that only a small part of this acid was reduced before 0.20 per cent acidity of the

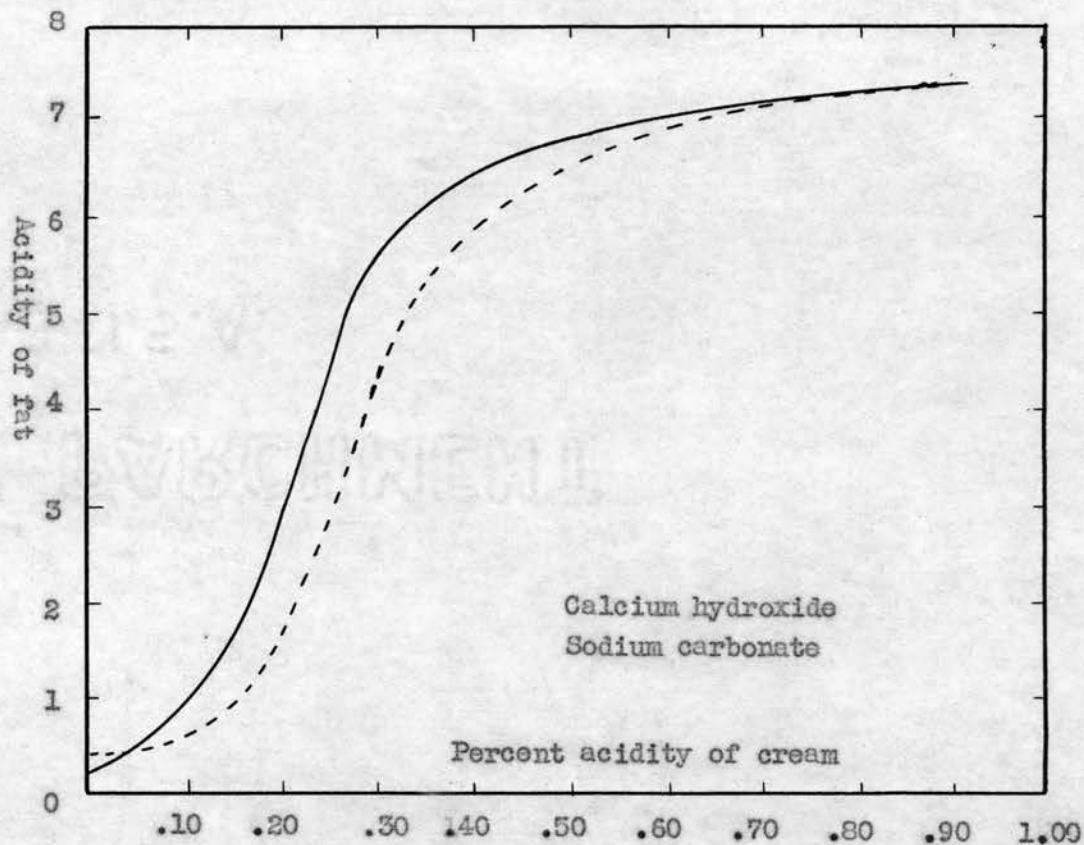


Figure 9. Effect of Neutralization of Cream With Calcium Hydroxide and Sodium Carbonate Upon Fat Acidity Which Was Increased by Addition of Palmitic Acid

cream was reached. According to Rogers (12), oleic acid comprises an average of 31.895 per cent of the fatty acids of butterfat. A comparison of the resistance of oleic acid and that of a mixture of acids used in this problem (mixed in proportions based upon the averages found by Holland et. al. (10) to occur in butterfat) indicate the great influence of oleic acid upon the resistance of the fatty acids as a whole. This mixture was approximately 34.5 per cent oleic acid.

Comparative Effectiveness of Calcium Hydroxide and Sodium Carbonate

Chemically pure calcium hydroxide and sodium carbonate were the two neutralizers used in this problem. These two neutralizers were chosen because they are representative of the two types of neutralizers in

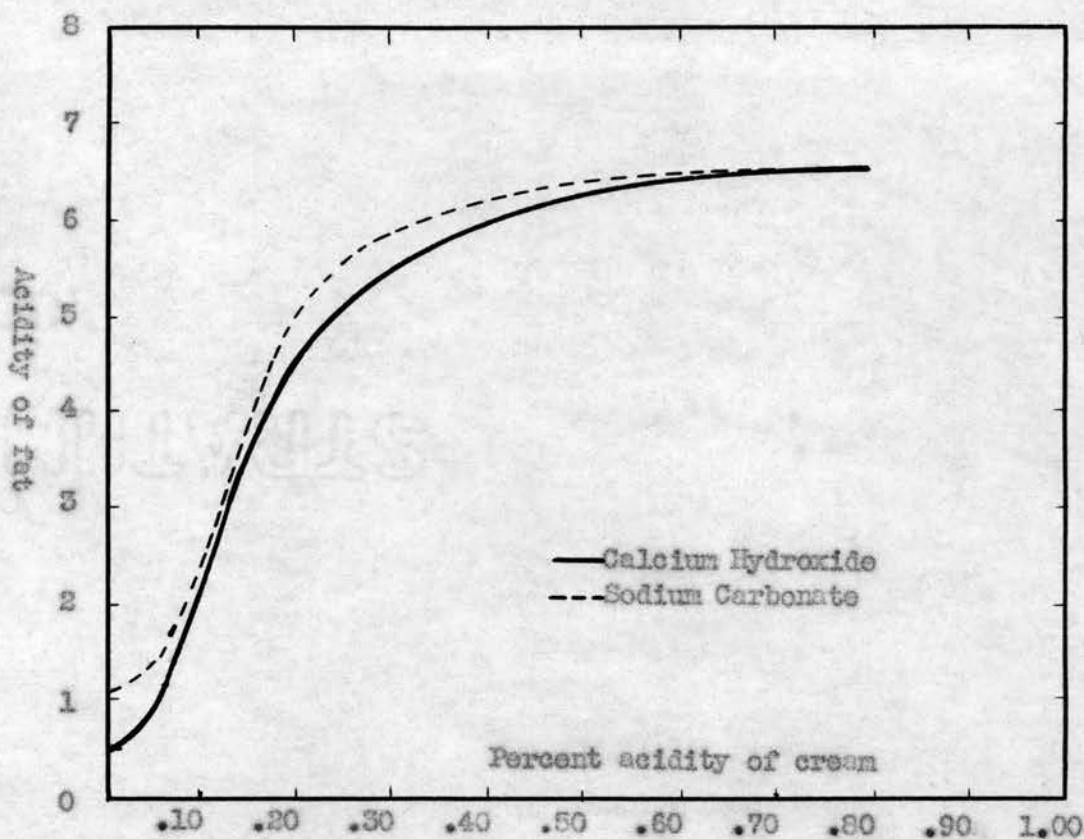


Figure 10. Effect of Neutralization of Cream With Calcium Hydroxide and Sodium Carbonate Upon Fat Acidity Which Was Increased by Addition of Oleic Acid

general commercial use. Gould and Tomley (9) made a rather extensive study of the effectiveness of several types of commercial neutralizers upon the reduction of the fatty acids. They concluded that, in general, the soda neutralizers were more effective in reducing fat acidities than were the lime neutralizers at points above 0.05 per cent acidity of the cream. Their data show that a somewhat greater percentage of the fatty acids were reduced by the limes than by the sodas at the neutral point in all cases except the ones in which caustic soda was used. The data herein presented agree very favorably with these conclusions in all series except that of oleic. In this series, the calcium neutralizer was more efficient than the soda.

Sodium carbonate was a little more effective than calcium hydroxide in the reduction of the acids of Group I, however, both neutralizers did well in reducing these acids. Figure 8 shows that sodium carbonate reduced caproic acid more rapidly than did calcium hydroxide. At 0.30 per cent acidity of the cream, about 12 per cent more caproic acid was reduced by the soda than by the lime.

A comparison of butyric and caproic acids of Figure 5 with the same acids of Figure 7 shows that both neutralizers were equally efficient with respect to equivalent weights.

The method for determining the effectiveness of the two neutralizers on an equivalent weight basis was to determine the per cent of the fatty acid reduced by a known amount of neutralizer; then to plot this percentage against the various fractional parts of the equivalent weights of neutralizer. This being done, the per cent of the fatty acid reduced by a given fractional part of an equivalent weight was read directly from the curves in compiling the data of Table V. The molecular weight of calcium hydroxide is 74 and sodium carbonate is 106. Since both neutralizers are bivalent, the equivalent weight of calcium hydroxide is 37 and sodium carbonate, 53.

The difference in the effectiveness of calcium hydroxide and sodium carbonate in neutralizing the fatty acids of Group II was somewhat greater than it was in Group I. The sodium carbonate was a little more effective in reducing this group of acids within the normal range of neutralization. At the neutral point, however, the lime was more effective than the soda. This is clearly shown in Figure 9, which is representative of all the acids of Group II.

Table V and Figures 5 and 7 show that in the case of the same number of equivalent weights, the soda was much more effective until large amounts of each neutralizer were added. As the amounts increased, the lime became more effective on the equivalent weight basis. These differences are very likely due to physical and chemical differences between the two neutralizers; such as solubility in water and the ability to combine with certain constituents of cream. Sodium carbonate is highly soluble in water while calcium hydroxide is only slightly soluble. Calcium hydroxide combines with casein in appreciable amounts while sodium carbonate does not.

In Group III, or the oleic series, sodium carbonate was less efficient than calcium hydroxide in reducing this acid, while in the other two groups, it was more efficient. From an acidity of 0.10 per cent in the cream down to the neutral point, the superiority of the lime over the soda was very evident, as will be noted in Figure 10. In the case of the same number of equivalent weights, the sodium carbonate was more effective than calcium hydroxide in reducing oleic acid until large amounts of each neutralizer were used. Even though the lime was superior to the soda, its efficiency in the reduction of this acid was not satisfactory since a very small per cent was reduced at the lower limit of cream neutralization under commercial conditions.

CONCLUSIONS

Butyric acid offered little resistance to neutralization by either calcium hydroxide or sodium carbonate.

Caproic acid offered slightly more resistance than butyric acid to neutralization. Calcium hydroxide was a little less efficient than sodium carbonate in reducing this acid.

All the saturated fatty acids of molecular weights higher than caproic acid that were used in this study offered considerable resistance to neutralization. Sodium carbonate was more effective than calcium hydroxide in the neutralization of these acids within the normal range of neutralization.

Oleic acid offered the greatest resistance to neutralization of all the acids used in this study. Calcium hydroxide was more efficient in the neutralization of this acid than sodium carbonate.

Larger fractional parts of equivalent weights of calcium hydroxide than sodium carbonate were required to neutralize the same percentage of either of the fatty acids studied. This is probably due to the fact that calcium combines with the casein of milk in appreciable amounts while soda does not.

The resistance offered to neutralization by a mixture of the fatty acids used in this study falls between that of the higher molecular weight saturated fatty acids and that of oleic acid. This indicates that oleic acid is largely responsible for the resistance to neutralization offered by the fatty acids in butterfat.

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