FATTY ACIDS

FOR

CHEMICAL SPECIALTIES

A symposium of the Soap, Detergents and
Sanitary Chemical Products Division of the
Chemical Specialties Manufacturers Association

1955

Reprinted for
FATTY ACID DIVISION — SOAP ASSOCIATION

FATTY ACID SYMPOSIUM

Soaps, Detergents and Sanitary Chemical Products Division of the CSMA

Moderator: DR. D. H. TERRY
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New York, New York

OPENING REMARKS

Mr. Chairman, Ladies and Gentlemen, the subject to be discussed this morning is "Fatty Acids."

For many, many years Fatty Acids have been the main ingredients in the production of all types of soaps. The soap industry is one of the oldest in America, and has been and continues to be a very important economic factor in our everyday living.

The uses of soap have become innumerable and varied. Its largest market is in the home, where its chief uses are as toilet soap and as laundry soap. There are, however, very many industrial applications for soap because of its wetting, emulsifying and cleansing powers. Soap is now found in many commercial processes.

Over the past five years soap requirements, sales, and production have slowly decreased. This has also reflected a decreasing requirement for fatty acids, since they are the basic ingredient in soap production.

In view of this decline in the requirements for fatty acids, many companies have spent considerable time and effort in research and market development to develop new outlets, uses and applications for fatty acids. In this investigation many new and interesting developments have been uncovered in regard to fatty acids.

Approximately five years ago this division sponsored a symposium on fatty acids. In view of the more recent developments on fatty acids, it was felt worthwhile to have another panel discussion on these materials.

The purpose of this symposium, organized through the combined efforts of the Market Development Committee of the Fatty Acid Division of the Soap Association, and the Soaps, Detergents and Sanitary Chemicals Division, is to convey to the members of the CSMA all the latest information available on fatty acids.

We wish to thank Mr. Scott Pattison, Manager of the Fatty Acid Division of the Soap Association, Mr. B. W. Schroeder, Chairman CSMA Sub-Committee, Fatty Acid Division of the Soap Association, and other members of the Soap Association for their excellent cooperation and assistance in arranging this panel discussion.

The topics to be discussed by the panel members were selected so that fatty acids would be covered completely from their basic chemistry to their end uses in special products.

The panel members were selected from the major producers of fatty acids and chemical specialties. They are all experts in this field.

I would now like to introduce the panel members. First, Dr. H. C. Black of Swift and Company, who will speak on the "Basic Chemistry of Fatty Acids"; Dr. H. Wittcoff of General Mills, Incorporated who will discuss the "Properties of Fatty Acids and Analytical Methods"; Dr. M. R. McCorkle of Armour and Company, who will cover "Reaction Products of Fatty Acids"; Dr. George Zinzalian of E. F. Drew and Company who will speak on "Storage and Handling of Fatty Acids"; Mr. R. D. Aylesworth of Emery Industries, Incorporated whose subject will be "Requirements of Fatty Acids used in Liquid and Metallic Soaps"; and Dr. H. Lederer of R. M. Hollingshead Corporation who will conclude the formal presentation part of this program with a paper on "Requirements of Fatty Acids used in Other Chemical Specialty Products."

In order to keep the meeting running without any interruption, the six speakers will give their papers in the order introduced. After the last paper has been completed, there will be a short recess during which we will collect the forms which were handed to you as you came in. Please write any questions you wish to ask, the name of the panel member to whom you want it directed, and your name and company. If you do not direct it to any one person, then we will try to dispose of it as best we can. I also want to suggest that there is no rule in this panel against panel members' asking each other questions.

Now I would like to proceed with the more interesting part of the program by introducing the first speaker at this time.

BASIC CHEMISTRY OF FATTY ACIDS

by H. C. BLACK
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Swift & Co., Chicago, Ill.

INTRODUCTION

The basic structure of fats was established nearly a century and one-half ago when Chevreul found that they were composed of fatty acids and glycerol. A little later Gusserow separated saturated from unsaturated acids by differential solubilities of their lead salts. Even though many significant and brilliant discoveries were made during the nineteenth century, the fats and fatty acids were sadly neglected until the beginning of the twentieth century. They were not attractive research materials because they were not readily crystallizable and few crystalline derivatives could be prepared. In spite of the lack of basic chemical knowledge during the nineteenth century, much empirical information accumulated permitting establishment of the consuming industries such as food, soap, paints and varnishes. There was no surplus as we have had recently. In the past two decades, much work has been done and many articles and numerous good books on fats and fatty acids have been published. We know the structure of the great majority of the known fatty acids and have information as to how to prepare and make practical use of many of their derivatives in our expanding chemical era.

SOURCES

Fats are essential constituents of all forms of plant and animal life, and are consequently widely distributed. However, the plants and animals that produce oils and fats in sufficient quantity to constitute a significant source are few. The largest of these comprises the annual plants such as flax, soybean, cotton, peanut and castor bean. These grow in temperate climates requiring cultivation. Production can be varied. The second source of vegetable oils is the oil bearing trees such as coconut, palm, olive, and tung. These grow in the warm or temperate climates.

The commercial land animal fats come largely from hogs, sheep and cattle. Milk fats are nearly all used for food. The sea contributes a considerable volume of oil. Among the most important sources are sardine, menhaden, herring and whale, including sperm whale.

CHEMISTRY

Fatty acids are present in fats and oils as glycerides or esters of glycerol except in sperm oil, where some of the fatty acids are esterified with fatty alcohols, mainly cetyl alcohol. The fatty acids are released by hydrolyzing ester linkage. This is done by chemically adding water, a process commonly referred to as fat splitting. The most common methods are the Twitchell, autoclave, and continuous methods. In the Twitchell process a catalyst speeds up the reaction as the fat is heated with boiling water. The autoclave method depends on heat to speed the reaction. The continuous method also relies on heat, and is carried out by passing water and fat countercurrently through a tower.

The fatty acids resulting from the splitting operation can be used as such or further processed to remove non-fatty acid constituents, and fractionated by distillation or selective solvent extraction. They may be fractionally crystallized by chilling and pressing, or by the use of solvents. New techniques still in the experimental stage for separation are molecular diffusion and the use of urea or thiourea to form complexes.

FATTY ACIDS

The natural fatty acids are generally aliphatic compounds with a carboxyl group at the end of a straight carbon chain. Nearly all of them have an even number of carbon atoms. The acids differ from one another in the number of carbon atoms and the number and position of the double or unsaturated bonds.

SATURATED ACIDS

The saturated acids contain no double bonds. They vary in chain length from butyric, which contains four carbon atoms, to lignoceric, which has 24. Table I shows the common saturated acids. At room temperature the shorter chain length acids are liquid. Lauric and all longer chain acids are solids at room temperature. The most widely distributed and the most commercially important are palmitic and stearic acids. Commercial stearic acid in its different grades consists of roughly equal parts of these two acids.

TABLE I

Saturated Acids

Common Name	Number of Carbon Atoms	Geneva Name
Butyric	4	Butanoic
Caproic	6	Hexanoic
Caprylic	8	Octanoic
Capric	10	Decanoic
Lauric	12	Dodecanoic
Myristic	14	Tetradecanoic
Palmitic	16	Hexadecanoic
Stearic	18	Octadecanoic
Arachidic	20	Eicosanoic
Behenic	22	Docosanoic
Lignoceric	24	Tetracosanoic
Cerotic	26	Hexacosanoic

UNSATURATED ACIDS

These acids, particularly the highly unsaturated members, are not as well characterized as the saturated acids because of the difficulties in isolating them. Also, changes can occur during separation and identification.

The unsaturated acids differ from one another in the number of carbon atoms, the number of double bonds, the position of the double bonds, and the geometry of the double bonds. All of the unsaturated acids, with the exception of elaidic, are liquid at room temperature.

TABLE II

Unsaturated Acids

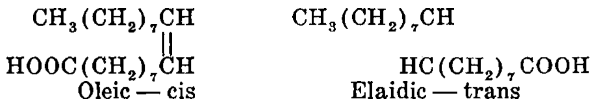
(Monoethylenic)

Common Name	Number of Carbon Atoms	Geneva Name
Obtusilic	10	9:10 Decenoic
Caproleic	10	4:5 Decenoic
Lauroleic	12	9:10 Dodecenoic
	12	4:5 Dodecenoic
Myristoleic	14	9:10 Tetradecenoic
	14	4:5 Tetradecenoic
	14	5:6 Tetradecenoic
Palmitoleic	16	9:10 Hexadecenoic
Oleic	18	9:10 Octadecenoic
Petroseleric	18	6:7 Octadecenoic
Elaidic	18	trans 9:10 Octadecenoic
Vaccenic	18	trans 11:12 Octadecenoic
Gadoleic	20	9:10 Eicosenoic
Erucic	22	13:14 Docosenoic

Table II shows the common fatty acids with one double bond. When one double bond exists, it can be between any two of the carbons except the first and second. However, only a few of the possible positions are found in nature. In addition, at any double bond, it is possible to have two geometric isomers referred to as cis-trans isomers. Table III represents this. Oleic acid is cis, and elaidic acid is trans.

TABLE III

Cis-Trans Isomers



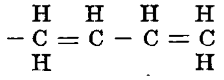
$$\begin{array}{r} CH_3(CH_2)_7CH \\ \| \\ HOOC(CH_2)_7CH \end{array} \qquad \begin{array}{ll} CH_3(CH_2)_7CH & \\ \| & \\ & HC(CH_2)_7COOH \end{array}$$

Oleic — cis   Elaidic — trans

In the case of acids with two or more double bonds, the double bonds may have no carbon atoms or several carbon atoms between them. A case where no carbon atoms separate the double bonds is referred to as a conjugated system. This is represented in Table IV. We may have more than two

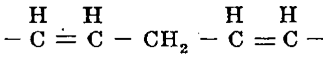
TABLE IV

Position of Double Bonds



$$\begin{array}{cccc} H & H & H & H \\ -C = & C - & C = & C \\ H & & & H \end{array}$$

Conjugated



$$\begin{array}{ccccc} H & H & & H & H \\ -C = & C - & CH_2 - & C = & C - \end{array}$$

Non-conjugated

double bonds in a conjugated system. Di and poly unsaturation imparts much faster reaction rates than one double bond. The conjugated system in fatty acids, as in other organic compounds, greatly increases the reactivity, and conjugated fatty acids undergo chemical reactions very similar to those of conjugated systems in general. Table V shows some of the di, tri and poly unsaturated acids.

TABLE V

Unsaturated Acids

(Di & Tri & Polyethylenic)

Common Name	Number of Carbon Atoms	Number of Double Bonds	Geneva Name
Linoleic	18	2	9:10, 12:13 Octadecadienoic
	22	2	9:10, 12:13 Docosadienoic
Hiragonic	16	3	6:7, 10:11, 14:15 Hexadecatrienoic
Linolenic	18	3	9:10, 12:13, 15:16 Octadecatrienoic
Elaeostearic	18	3	9:10, 11:12, 13:14 Octadecatrienoic
Parinaric	18	4	9:10, 11:12, 13:14, 15:16 Octadecatetraenoic
Moroctic	18	4	4:15, 8:9, 12:13, 15:16 Octadecatetraenoic
Arachidonic	20	4	5:6, 8:9, 11:12, 14:15 Eicosatetraenoic
Clupanadonic	22	5	Docasapentaenoic

In the partial hydrogenation of unsaturated fatty acids, many isomers may be produced. One or more of the double bonds in any of the various positions may be hydrogenated. The double bonds may shift positions or be converted to the trans form if not hydrogenated.

TABLE VI

Fatty Acids of Unusual Structure

Common Name	Number of Carbon Atoms	Structure
Tariric	18	Triple bond between 6 and 7th carbons.
Ricinoleic	18	12—hydroxy 9:10 Octadecenoic
Licanic	18	4—keto 9:10, 11:12, 13:14 Octadecatrienoic
Hydnocarpic	16	Closed 5 membered ring at end of carbon chain.
Chaulmoogric	18	Closed 5 membered ring at end of carbon chain.

Table VI shows several fatty acids of unusual structure. Ricinoleic acid is the principal acid in castor oil. On dehydration, a good portion of conjugated linoleic acid is produced. This accounts for the good drying properties of dehydrated castor oil. Licanic acid occurs in oiticia oil. It has three conjugated double bonds and a ketone group.

SUMMARY

In addition to their economical importance, the fatty acids are a versatile and interesting group of organic compounds.

THE RELATIONSHIP OF USE OF FATTY ACIDS TO THEIR PROPERTIES AND TO ANALYTICAL METHODS

by WILLIAM S. BALDWIN and HAROLD WITTCOFF
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Minneapolis, Minn.

Delivered by DR. HAROLD WITTCOFF

When Chevreul discovered, over a century ago, that tallow could be split chemically to yield glycerol and fatty acids, he brought untold relief to millions of people. For heretofore candles had been made from tallow, and in the process of burning the glycerol decomposed to acrolein, a tear gas which caused no end of discomfort. Following Chevreul's discovery, on the other hand, candles could be made from the more innocuous fatty acids, And once again we have an example of how technology made living more pleasant.

During Chevreul's lifetime—he reached the 100 mark—fatty acids found many uses beyond the candle industry. But without a doubt, Chevreul would be very much amazed, were he to view the list of current uses for fatty acids which have been tabulated in Table I. He would be even more amazed to know that in the United States alone, around 400 million pounds of fatty acids are produced for sale yearly. These fatty acids come from diverse sources — animal fats such as tallow, the vegetable oil "foots" which are a by-product of the edible oil refining industry, tall oil which is a by-product of the Kraft paper industry, vegetable oils such as coconut and castor, and marine oils—to mention the most important.

It is the purpose of this paper to describe the specifications, characteristics and properties of a few of the most widely used types of fatty acids. Thereafter these properties will be related to the analytical methods which are used to define specifications.

One is impressed immediately by the fact that the numerous uses for fatty acids indicated in Table I require products

TABLE I

Uses of Fatty Acids

Alkyds and Protective Coatings
Lubricants and Greases
Rubber Formulation
Textiles
Soap
Cosmetics
Flotation
Candles
Metal Working
Plasticizers
Resins
Pharmaceuticals
Printing Inks
Glues
Waxes
Leather Treating
Hydraulic Brake Fluid
Adhesives
Insecticides
Chemical Derivatives
Emulsifiers
Chewing Gum
Shortening Substitutes
Disinfectants
Incendiary Bombs
Fungicides
Germicides
Animal Dips
Insect Repellents
Driers
Catalytic Agents
Buffing Compounds
Core Oils
Cutting Oils
Quenching Oils
Mold Lubricants
Rust Preventatives
Wire Drilling Compounds
Paper Coatings
Paper Sizings
Caulking Compounds
Putties
Cements
Synthetic Detergents
Waxes
Polishes
Brake Linings
De-emulsifiers
Gels
Wax Crayons
Ammunition

with widely varying specifications. Obviously in this paper we cannot examine each of the several dozens of acids which are produced commercially. Rather, we have chosen a few important applications for fatty acids and will examine the properties of the fatty acids used in these applications. Thereafter, as indicated above, the analytical methods which are used to determine these properties will be discussed.

TABLE II
Some Major Uses of Fatty Acids

Field of Application	Pounds Consumed in 1952*
Alkyds	58 million
Soap	70 "
Chemical Derivatives	30 "
Lubricants	19 "
Rubber	35 "
Cosmetics	5 "

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* Figures estimated from U. S. Department of Commerce publications.

ALKYD RESINS

As reference to Table III will indicate, over one-half billion pounds of alkyd resins are produced yearly. Although the bulk of the alkyds manufactured in this country are based on oils, it is generally agreed that the most uniform products are based on fatty acids. Reference to Table II indicates that fatty acid usage for alkyds amounted to 58 million pounds in 1952. Of these 33 million pounds of acids, the largest percentage were of vegetable origin, and were characterized by an iodine value of 115 to 145. Of this group, the bulk of the acids had an iodine value in the range of 130. A smaller percentage had an iodine value below 130, but above 100.

TABLE III
Alkyd Resin Production[1]
1948-1953

Year	Millions of Pounds (dry basis)[2]
1948	288.3
1949	319.6
1950	417.1
1951	461.6
1952	458.4
1953	509.9[3]

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[1] Source: U. S. Tariff Commission.
[2] Includes resins, plasticizers, extenders, fillers, coloring agents and stabilizers. Also includes styrenated alkyds.
[3] Partial estimate.

The alkyd industry has always used tall oil for low grade products. However, highly refined tall oil acids with very low rosin contents are now available, and these too are finding a home in the alkyd industry. Undoubtedly their use for this purpose will increase markedly within the next five years. Finally, the alkyd industry uses some saturated acids, primarily lauric acid and coconut acids, principally in baking alkyds.

The typical specifications for a fractionally distilled vegetable acid widely used for alkyd manufacture follow.

Iodine Value	130-134
Acid No.	197-202
Saponification No.	197-203
Color (Gardner)	4 max.
Titer, °C.	26.0 max.
% Moisture	0.1 max.
% Unsaponifiable	2.0 max.

Acid Composition (approx.)

Palmitic	11%
Stearic	4%
Oleic	29%
Linoleic	51%
Linolenic	5%

A less expensive acid for alkyd production has the typical specifications listed below.

Iodine Value	110-122
Acid No.	195-202
Saponification No.	195-203
Color (Gardner)	7 max.
Titer, °C.	27.0-31.0
% Moisture	0.1 max.
% Unsaponifiables	2.0 max.

Acid Composition (approx.)

Palmitic	8%
Stearic	3%
Oleic	47%
Linoleic	42%

As indicated above, distilled, highly refined tall oil acids are of increasing importance in the alkyd industry. A typical tall oil acid has the following specifications.

Iodine Value	120-130
Acid No.	192-198
Saponification No.	192-199
Color (Gardner)	5-8
Titer, °C.	1.0-10.0
% Moisture	0.1 max.
% Unsaponifiables	2.0-2.5
% Rosin Acids	1.5-3.0

Acid Composition (approx.)

Palmitic	2%
Stearic	1%
Oleic	48%
Linoleic	47%
Rosin Acids	2%

It will be noted that a specification for rosin acids is inserted here, and this of course is because a slight amount of rosin is bound to occur in acids from tall oil sources. Improved processing procedures, however, promise to yield acids with less than 1 per cent of rosin.

The saturated acids used in alkyds are typified by coco acids and by relatively pure lauric acid. The specifications for each of these are listed below:

Specification	*Whole Coco Acids*	*Lauric Acid*
Iodine Value	5-15	1.0 max.
Acid No.	255-270	278-281
Saponification No.	255-270	278-282
Color (Gardner)	2 max.	1 max.
Titer, °C.	22.0-28.0	41.0-44.0
% Moisture	0.1 max.	0.1 max.
% Unsaponifiables	0.2-1.0	0.1-0.5
Acid Composition (approx.)		
Caprylic	8	....
Capric	7	2
Lauric	49	95
Myristic	17	3
Palmitic	9	....
Stearic	2	....
Oleic	6	....
Linoleic	2	....

ANALYSES OF IMPORTANCE FOR ALKYD-TYPE ACIDS

IODINE NUMBER is, of course, an indication of the unsaturation of the fatty acid. In a straight oil—that is, a glycerol ester iodine number is an indication of how fast the oil will dry. Thus linseed oil, with its higher iodine number, dries faster than soybean oil, which, because of its lower iodine number, actually never reaches a completely tack-free stage. In a more complex and more highly functional system such as an alkyd resin, iodine number cannot be related linearly to drying time since other factors related to functionality, such as the type of polyhydric alcohol and the oil length of the alkyd, also contribute to drying time.

Iodine number is defined as the centigrams of iodine absorbed by one gram of fatty acid. It is determined in routine fashion by one of several procedures. A convenient method is the socalled rapid Wijs, details for which will be found in the standard methods of the American Oil Chemists' Society.[1]

This method provides erroneous results if some of the double bonds in the fatty acids are conjugated. The Woburn[2] method has been devised to overcome this difficulty.

ACID NUMBER is defined as the number of milligrams of potassium hydroxide required to neutralize the fatty acids present in one gram of material. It is a measure of the free fatty acid groups present. For fatty or rosin acids, a simple titration with alkali to a phenolphthalein end point is used, and this is described in the American Oil Chemists' Society standards.[3] From this same determination, the neutral equivalent of the acid may be determined simply by a different type of calculation. Neutral equivalent is essentially the molecular weight of the acid if it is free from non-acid impurities.

SAPONIFICATION NUMBER is defined as the milligrams of potassium hydroxide required to saponify one gram of sample. It is a measure of the free fatty acids plus any material which will be saponified or which will convert to soap under the conditions of the analysis. Saponification value is determined in routine fashion as described in the official standards of the American Oil Chemists' Society.[4] If the acid is free of esters, the acid number and the saponification number will be the same. If esters are present, the saponification number will be higher than the acid number. If glyceride is present, the difference between acid number and saponifiaction number is a rough measure of the glycerol present. The folowing empirical equation is used to estimate glycerol content:

$$(\text{Saponification No.} - \text{Acid No.}) \times 0.0547 = \%\ \text{glycerol}$$

UNSAPONIFIABLE CONTENT is defined as the per cent of those materials which cannot be saponified by alkali, but which are soluble in ordinary fat solvents. Included in this definition are higher aliphatic alcohols, sterols, pigments and hydrocarbons. The determination is carried out according to American Oil Chemists' Society standards.[5] Unsaponifiable content is low in high grade acids.

PER CENT MOISTURE is defined as the per cent of material which is volatile under the conditions specified by the test being used. There are three methods described in the American Oil Chemists' Society standards[6] which may be used for this determination. They differ primarily in the temperature and equipment used, and the choice of test depends on the nature of the material being analyzed.

TITER is defined as the solidification temperature of fatty acids. It is determined routinely by an American Oil Chemists' Society standard method.[7] The method involves hydrolysis, if necessary, to obtain the fatty acid, followed by determination of the solidification temperature of the acid. Very roughly, titer is an indication of saturated acid content of the fatty acid composition. The relationship is far from linear, however, and a high titer does not necessarily mean that the acid will not perform properly in an alkyd formulation. Actually, an acid with a high titer because of relatively high saturated acid content may have a very high content of linoleic acid. Thus, it would perform better than a low titer acid which had very little saturated acid, but which had a low content of linoleic acid and a high content of oleic acid. This follows since linoleic acid is a drying acid, whereas oleic acid is not a drying acid, although oleic acid, if impure, may have a low titer.

COLOR is a very important specification for fatty acids to be used in alkyds. Several methods are available for determining color. One of the most common and most widely used in the Gardner (1933) method which is described in the American Oil Chemists' Society standards.[8] In this method the color of the fatty acid is determined by comparison with standards of definite color composition, and the results are reported in arbitrary numbers.

The Lovibond[9] method for determining color is somewhat more time consuming, and is based on the principle that the color in oily materials is largely a combination of red and yellow. Accordingly, the color of a test sample is compared with standard red and yellow glasses. Each standard has a numerical value, and the color is reported according to these numbers.

The F.A.C.[10] procedure for determining color is ordinarily not used with alkyd acids, but is used with acids intended for the grease and lubricant field. This method is similar to the Gardner method, where a sample is compared with standard color tubes. It is ordinarily used for acids which are too dark to be judged on the Lovibond scale.

A photometric method for color determination is described in official Oil Chemists' Society standards.[11] Such a procedure is important for acids of excellent color, and is generally used where the acid has a Gardner color of one or better. In this method the optical density of the sample is determined at four specified wave lengths by means of a Coleman, Jr. spectrophotometer. These values are then substituted in an equation to calculate a numerical value for the color of the oil.

COLOR STABILITY is an important property of acids to be used for alkyd manufacture. Alkyds are manufactured at temperatures in the region of 200-250°C., and thus it is important that acids subjected to such temperatures have good color stability. Also, once the alkyd has been prepared and has been laid down as a protective coating, in the form of a film, it is important that the fatty acid contribute to the over-all color stability of the alkyd film. To date no standard method has been accepted for determining color stability, and difficulty has been experienced in correlating tests with actual performance. One alkyd manufacturer has a color stability test actualy based on the production of a small pilot batch of alkyd resin.

Color stability tests in use today depend upon measurement of the color of the fatty acid before and after the acid has been subjected to a period of heating under specified conditions. Such tests are applied not only to unsaturated acids for use in alkyds, but also to saturated acids. For saturated acids, color degradation is best measured by spectrophotometric methods, and wave lengths for measurement must be chosen so that the most significant type of information is obtained. If the acid is unsaturated, color degradation is sufficiently severe so that meaningful results are obtained if the color is measured by the Gardner or Lovibond procedures. Fatty acid manufacturers employ such stability tests as control measures, although, as indicated above, no standard method has yet been accepted.

Several procedures have been proposed for determining color stability. A.S.T.M. is currently considering two of these. One involves heating the sample in an adequately controlled oil bath at 205°C. for one hour and thereafter determining the color of the hot sample. The second method involves rapid heating of the sample to 250°C., followed by a normal gradual downheat of the sample in the oil bath to about 100°C., prior to determining the final color.

ROSIN ACID CONTENT is an important specification, as already indicated, for acids derived from tall oil sources. Rosin acid content can be determined by an A.S.T.M. standard method[12] which depends on the fact that fatty acids will esterify readily with methanol in the presence of sulfuric acid, whereas rosin acids will not. Accordingly, it is possible to esterify preferentially and then to determine the rosin acid content by direct titration. Certain inherent inaccuracies accompany this method.

Acid Composition

The specifications described above are far from a precise indication of fatty acid composition. Although iodine number, for example, is certainly an indication of the degree of unsaturation present, it provides no indication of *which* unsaturated acids are present. Thus, a composition which is essentially pure oleic acid will have an iodine number of 90, and a composition consisting of approximately equal parts of stearic and linoleic acids will also have an iodine number of approximately 90. As already indicated, titer is an indication of saturated acid content, but no direct relationship exists. Acid number may indicate chain length, since acid number increases as average molecular weight decreases. Again, however, extraneous factors such as non-acid impurities make it virtually impossible to derive direct information regarding fatty acid composition from acid number.

Accordingly, the only procedure for determining fatty acid composition precisely is one of actual distillation. Either the methyl esters or the free acids may be distilled in a column which is sufficiently sensitive to fractionate fatty acids according to molecular weight.

The requirements for a column for analytical distillation of fatty acids include the following:

1. A minimum of 15 to 20 theoretical plates.
2. Nearly perfect adiabatic conditions so that heat loss of the column will be low and flooding will be prevented.

Fractional distillation has been used extensively as a research tool to determine the composition of fatty mixtures from various oils. It is time consuming and difficult, and thus has not become a routine analytical method. The tendency toward more rigid specifications for fatty acids is such, however, that fatty acid composition could well become an established specification. Useful laboratory columns for the vacuum distillation of fatty acids include the Whitmore, Todd and Podbielniak columns. Fatty acid distillation has been discussed by Norris and Terry[13] and forms the basis for a Toilet Goods Association standard method.[13]

Obviously, the bulk of most fatty acid compositions are C_{19} acids with varying degrees of unsaturation. Distillation will not separate stearic, oleic, linoleic and linolenic acids. Accordingly, other procedures are required in order to determine the exact composition of the C_{18} fraction of the fatty acid mixture. Saturated acid content can be determined by a procedure published by Earle and Milner.[14] This procedure is based on the fact that saturated acids may be removed by crystallization from acetone at low temperatures. The method is applicable to fatty acids from soybean and cottonseed sources, but cannot be used on highly unsaturated oils such as perilla oil, or oils which contain very large amounts of oleic acid. If unsaponifiables are present to the extent of 2 per cent or more, these should be removed before carrying out the determination. In this procedure the saturated acids are crystallized and an iodine value determination is used to correct for any contamination by oleic acid.

Oleic, linoleic and linolenic acids are determined by a spectrophotometric procedure. Although none of these three acids absorb in the ultraviolet region, the conjugated forms of linoleic and linolenic acids do absorb strongly in the ultraviolet. A dienoic (from linoleic) acid absorbs at 233 mu. A trienoic (from linolenic) acid absorbs at 268 mu, whereas a tetraenoic acid absorbs at 315 mu. In the standard procedure for this determination[15] the polyunsaturated acids are conjugated by heating them under specified conditions in a glycol bath in the presence of a specified amount of alkali. The transmission at the appropriate wave lengths is then determined as a direct measure of the conjugated polyunsaturated acids present. An appropriate blank is also run. Oleic acid is estimated from these data and iodine value. Unsaponifiable content frequently has a high iodine value and introduces error. Chromatographic techniques are also being studied for this separation.

In alkyd resin production, acids containing virtually no linolenic acid are preferred. Linolenic acid, which is a component of linseed oil, provides coatings with poor color stability. Thus, for white appliance or architectural enamels, where good color and good color stability are required, fatty acids from cottonseed and soybean sources are preferred, since such acid compositions contain virtually no linolenic acid.

LUBRICANTS AND GREASE

Reference to Table II indicates that very appreciable quantities of fatty acid are employed by the grease and lubricant industry. Most of these are tallow based acids, although stearic acid from vegetable sources is also used. Hydrogenated fish oils are used in small quantities. A specialty acid, 12-hydroxystearic acid, obtained from hydrogenated castor oil, is an important acid for lithium based greases.

Typical specifications for a fatty acid from tallow sources, used by the grease industry, follow:

Iodine Value	50- 60
Acid No.	197-205
Saponifiification No.	197-205
Color (Gardner)	9 max.
Titer, ° C.	39.0-43.0
% Moisture	0.1 max.
% Unsaponifiables	2.5 max.

Fatty Acid Composition (approx.)

Myristic	2%
Palmitic	26%
Stearic	16%
Oleic	48%
Linoleic	6%

All of these specifications have already been discussed in relation to fatty acids for alkyd manufacture. Analytical procedures are the same as indicated above.

It is important that acids used for greases have good oxidative stability. As with color stability, there is no agreement regarding a standard test for the oxidative stability of fatty acids. Accordingly, oxidative stability is not a specification listed by all fatty acid producers. Actually, most grease producers prefer to run an oxidative stability test, such as the Norma Hoffman test, on the final grease rather than on the fatty acids.

Certain oxidative stability tests, however, have been developed for fatty acids, and most of these depend upon the performance of a controlled oxidation, the results of which can be measured by various means. The Mackey test is a modification of a test described by Gardner.[16] In this test a weighed piece of cotton, surrounding a thermometer, is wet with a standard weight of the fatty material to be tested. The cotton and thermometer are then placed in an air bath at 100° C., and the time necessary for oxidation to reach a sufficient velocity to raise the temperature of the thermometer to 105° C. is recorded. There is ordinarily an induction period before oxidation starts.

The Swift stability test[17] is also a measure of oxygen uptake and is widely used on oils. It is not used to any great extent with fatty acids, although its application to fatty acids is probably feasible. The test depends on the achievement of a certain peroxide value when the material under test is heated at 90° C. and is subjected to a constant stream of air.

One fatty acid producer makes reference in his literature to an oxidative stability test in which the time is recorded for the sample to absorb 10 cc. of oxygen.

RUBBER APPLICATIONS

The rubber industry consumes large quantities of fatty acids, as reference to Table II will indicate. Mostly, saturated fatty acids are used as activators, accelerators and softening agents. Unsaturated acids are used in lesser quantities in foam and sponge rubber production. The saturated acids are ordinarily low grade stearic or split tallow materials, whereas the unsaturated acids are low grade oleic or tall oil acids.

The specifications for a typical rubber grade stearic acid follow:

Iodine Value	3-14
Acid No.	185-205
Color (F.A.C.)	3-11
Titer, ° C.	52.0-58.0
% Moisture	0.1 max.
% Unsaponifiables	2.0 max.
% Ash	0.3 max.

Fatty Acid Composition (approx.)

Palmitic	49%
Stearic	44%
Oleic	7%

The F.A.C. color procedure generally used with rubber grade fatty acids has been discussed above.[10] Ash content is a specification which has not appeared for alkyd or lubricant grade acids. The ash content of a distilled acid is naturally very low. It is included as a specification for rubber grade acids because low grade materials are generally employed in this highly competitive field. Ash content may be determined according to a standard American Oil Chemists' Society method.[18]

COSMETICS

In direct contrast to the rubber industry, which uses large quantities of low grade fatty acids, the cosmetics industry uses a much smaller quantity of high grade acids. These find application in such products as shaving creams, vanishing creams and lotions, deodorants and shampoos. Various grades of stearic acid, oleic acid, lauric acid and coco acids are used by the cosmetics industry. The published specifications for these acids frequently do not reflect the demands made by the cosmetics industry. Such properties as good color and low iodine value are important for saturated acids. Other important properties, often not reflected in manufacturers' specifications, include crystalline structure, coefficient of shrinkage, penetration and odor. Some of these properties have been discussed in an article by Peters and Clark.[19] These authors determined shrinkage, for example, by melting saturated acids in an oven at 80° C. in small straight-sided molds. These were then allowed to cool slowly in the oven. The per cent shrinkage was calculated by subtracting the diameter of the cooled cake from the diameter of the mold, dividing this figure by the diameter of the mold, and multiplying the resultant value by 100.

The degree of crystalline structure of a saturated acid or mixture of acids may be determined by inspection. As pointed out by Peters and Clark,[19] it has been found that for mixtures of stearic and palmitic acids, a definite crystal line range can be determined by inspection when the stearic-palmitic ratio is in the range of 40-60 to 50-50. When these limits are exceeded by even one per cent, a marked decrease in crystal structure may be observed. The presence of oleic and myristic acids does not appear to affect this crystalline range. These workers also observed that if stearic or palmitic acids are at least 90 per cent pure, a soft, large crystal is produced.

Hardness of fatty acids is usually determined by a penetration method, which is a standard A.S.T.M. test.[20] The Shore hardness procedure,[21] which is used primarily for waxes, may also be applied to fatty acids.

Odor is, of course, a subjective factor and can be rated quantitatively only by a highly experienced panel. In general, however, the producer strives to achieve what to the normal sense of smell is a "bland" odor.

TEXTILES

The textile industry uses fairly large quantities of fatty acids, largely in the form of derivatives. Because of the diversity of the industry and the numerous forms in which fatty acids are used, it is difficult to estimate volumes. The textile industry makes use largely of oleic acid, and various grades are available. These grades are distinguished mainly by oleic acid content, color, titer and polyunsaturate content. Typical specifications for three grades of oleic acid follow.

	High Grade	Intermediate Grade	Low Grade
Iodine Value	86-90	90-93	90-93
% Free Fatty Acid (as oleic)	100-102	98-101	93-97
Saponification No.	201-205	197-203	190-200
Color (Lovibond, 5¼″ cell)	5y/0.5R (max.)	15y/1.5R (max.)	....
Titer, ° C.	2-6	8-11	8-11
% Unsaponifiable	1.0 (max.)	1.5 (max.)	3.0 (max.)
% Polyunsaturate Content	5.0 (max.)	....	....

The textile industry is interested in acids of good color and good odor. Good oxidative stability is required together with low polyunsaturate content. Analytical procedures for determining these critical specifications have already been discussed above.

SUMMARY

This paper has outlined the specifications of several types of fatty acids which are widely used in a number of industries. An attempt has been made to explain the significance of these specifications, and the analytical procedures for determining these specifications have been described. It has not been the purpose of this paper to be all-inclusive. Rather the goal has been to point out the most widely used analytical procedures as they relate to the important uses of fatty acids.

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NITROGEN-CONTAINING DERIVATIVES OF THE FATTY ACIDS

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Delivered by DR. M. R. McCORKLE

The most promising, new markets for fatty acids probably lie in the direction of derivative formation. The fatty acids themselves are well known and their applications well exploited. The variety and versatility of their derivatives, however, constitute a challenge to the research and manufacturing chemist.

I should like to discuss just one phase—a still-developing phase—of the attack on this problem.

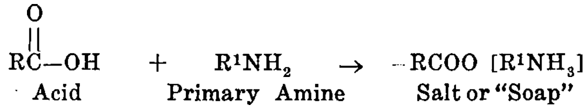
Leaving aside consideration of the simple, inorganic neutralization products of the fatty acids, the metallic soaps, the largest volume derivatives are the alcohols, the esters and the nitrogen-containing compounds. The alcohols probably constitute the largest single group of products, in their function as base materials for synthetic detergents, although much of this is captive production. The mono-and poly-esters of the fatty acids are probably next in tonnage produced, and are largely found as plasticizers, as surface-active agents, or as protective coating ingredients. The nitrogen-containing derivatives, those under discussion here, are next. Totalling about 60 million pounds of product in 1953, for surface-active uses alone, they more than doubled their production rate of 1948.

Although far from the leading volume consumer of fatty acids, this latter group does constitute one of the most versatile and interesting groupings—at least from a chemical standpoint.

The nitrogen is usually added to the molecule by reaction with, or by replacement of the carboxylic function. The resulting compounds are usually surface-active, combining the balance of a long-chain, hydrocarbon, hydrophobic "tail" with a polar, hydrophilic "head." They can be diversified as to mode of ionization. They can be classified as non-ionics, for example the ethylene oxide addition products of the unsubstituted amides; as anionics, by sulfation of the ethanolamides; or as cationics, characterized by the highly adsorbent amines and quaternary ammonium salts.

The nitrogen-containing derivatives may be divided, on the basis of commercial significance, into five major groups; the organic soaps, the amides, nitriles, amines and quaternary amonium compounds. I should like to examine each of these in turn, particularly from the standpoint of preparation and application.

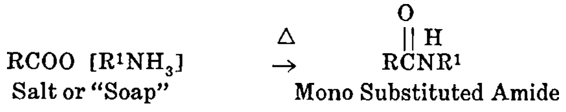
The fatty acids, as acidic compounds, can of course be neutralized by basic materials. The most common of the organic amines that have been used for this purpose are the mono-, di-, and triethanolamines, isopanolamine, morpholine, etc. The compounds formed by such reactions are simple neutralization products, prepared in solvent usually, but rarely isolated as such.



$$\underset{\text{Acid}}{\overset{O}{\overset{\|}{RC}}\text{—}OH} \quad + \quad \underset{\text{Primary Amine}}{R^1NH_2} \quad \rightarrow \quad \underset{\text{Salt or "Soap"}}{RCOO\ [R^1NH_3]}$$

They are, generally, prepared in *situ*, where needed, by a low temperature reaction in a one-to-one molar ratio of acid to amine. Their largest areas of application are as lubricating agents in rayon filament cone-winding or in wool spinning and weaving, as emulsifying agents in preparing resin emulsions, and in the cosmetic field, where they are characterized by the high-stability emulsions and soft creams they give in hair waving lotions, shampoos, etc. Their ability to be removed easily, by water rinsing usually, after serving their prescribed function is part of their value as emulsifiers, too.

The substituted amides are, at present, the largest representative class of nitrogen-containing compounds. The simplest approach to these derivatives is through certain of the organic amines just mentioned. Low temperature reaction gives neutralization, or salt formation. Elevated reaction temperatures, say 140-200° C., with the primary or secondary amines gives the mono- or di-substituted amides, respectively, with the resultant loss of a mol of water.

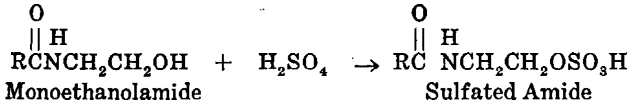


$$\underset{\text{Salt or "Soap"}}{RCOO\ [R^1NH_3]} \quad \xrightarrow{\Delta} \quad \underset{\text{Mono Substituted Amide}}{\overset{O\ \ }{\overset{\|\ H}{RCNR^1}}}$$

Six to seven hours of heating time is necessary to drop the free acid content to the few per cent level.

The simplest substituted amides are those prepared from a one-to-one molar ratio of acid to, e.g., mono- or diethanolamine. These are well defined compounds, essentially nonionic, useful in their own right or as chemical intermediates. Their major application is as additives to the better known alkyl sulfates or alkyl-aryl sulfonates. They function, here, as suds boosters and stabilizers, enhancing the effect of the base detergent. Tailor-making of these compounds, by balancing the hydrophobic "tail" (the length and unsaturation of the chain) and the hydrophillic "head" (the nature of the hydroxyl grouping around the amide function) will give a wide area of activity. Direction toward synergism with a specific detergent formulation can be arranged.

These hydroxy-substituted amides may also be further reacted to give anionic, sulfated products.

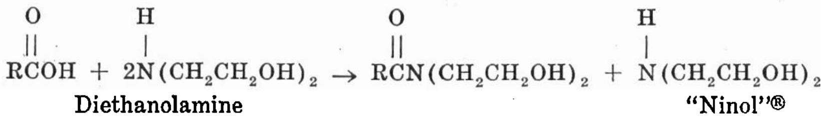


$$R\overset{\overset{O}{\|}}{C}\overset{H}{N}CH_2CH_2OH + H_2SO_4 \rightarrow R\overset{\overset{O}{\|}}{C}\,\overset{H}{N}CH_2CH_2OSO_3H$$

Monoethanolamide Sulfated Amide

This can be carried out by low temperature reactions (with or without solvent) with sulphuric acid, oleum or chlorsulfonic acid. These are excellent heavy-duty detergents in themselves, with good hard-water foaming characteristics and good sudsing properties. They are quite mild to the skin, compatible with soaps, and are used by the cosmetic chemist in shampoo formulations.

By varying the ratio of hydroxy-containing amine to fatty acid, the nature of the product is radically changed, from an essentially water insoluble product to a soluble one. A two-to-one ratio of diethanolamine to fatty acid, e.g., gives a mixture, of unknown chemical structure, that is an excellent primary detergent itself. This phenomenon will occur with several compounds of this type, giving rise to a class of products collectively called by the trade name "Ninols."

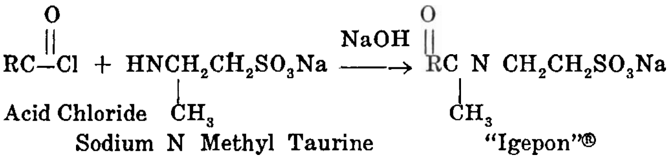


$$R\overset{\overset{O}{\|}}{C}OH + 2\overset{\overset{H}{|}}{N}(CH_2CH_2OH)_2 \rightarrow R\overset{\overset{O}{\|}}{C}N(CH_2CH_2OH)_2 + \overset{\overset{H}{|}}{N}(CH_2CH_2OH)_2$$

Diethanolamine "Ninol"®

They find rather wide application in liquid detergents, as emulsifying agents (in horticultural sprays, e.g.), as dye solvents in lipsticks, as pigment dispersing agents, as thickening agents for synthetic detergents or liquid soaps, as viscosity increasers in paste or cream preparation, as vat dye suspenders in textile dyeing and as shampoo ingredients.

Another major group of amide derivatives centers around the sulfonated amines typified by the "Igepon" type of compound. This involves the reaction between the fatty acid (usually in the form of the acid chloride) and a primary or secondary amine containing a sulfonic acid grouping in the molecule.

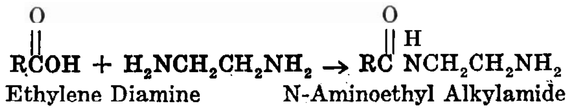


$$R\overset{\overset{O}{\|}}{C}-Cl + \underset{\underset{CH_3}{|}}{HN}CH_2CH_2SO_3Na \xrightarrow{NaOH} R\overset{\overset{O}{\|}}{C}\,\underset{\underset{CH_3}{|}}{N}\,CH_2CH_2SO_3Na$$

Acid Chloride Sodium N Methyl Taurine "Igepon"®

The resultant sulfonated amide, a typically anionic compound, can be varied in properties, again by balancing the polar and non-polar functions in the molecule. These compounds, in general, have excellent emulsifying, wetting and detergent properties, and are resistant to acid, base, hard water, and hydrolysis in neutral solution. Their uses include admixture with soaps to prevent lime soap deposition, as a levelling agent in dyeing textile fibers, in the kier boiling of cotton, in bleaching heavy cotton fabrics, in electroplating, in shampoos, as a detergent or detergent additive, etc.

The polyamines (ethylene diamine, diethyl ethylene diamine, etc.) also contribute to a distinctive class of amide derivatives, the so-called "Sapamines." These are prepared by reacting a mol of fatty acid with one amine of a polyamine molecule, leaving a free substituted or unsubstituted amine grouping in the final product.

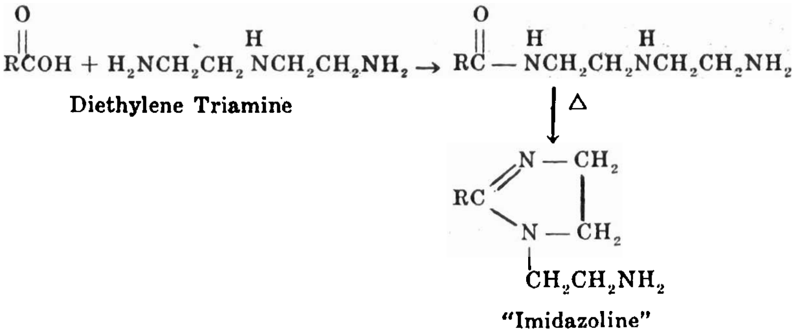


$$R\overset{\overset{O}{\|}}{C}OH + H_2NCH_2CH_2NH_2 \rightarrow R\overset{\overset{O}{\|}}{C}\,\overset{H}{N}CH_2CH_2NH_2$$

Ethylene Diamine N-Aminoethyl Alkylamide

These are now cationic agents, ionizing so that the long alkyl chain bears the positive charge. They are often used in the form of their salts, the neutralization products of the free amine function. Besides their general classification as emulsifying agents and detergents, they have found use as fabric softeners, levelling agents for dyes, in formulating shampoos, acid creams, etc.

Carried further, the polyamines contribute two other classes of nitrogen derivatives. Those with more than one primary or secondary amine can give polyamides with excess fatty acids. Those amido amines still with a free amino grouping can undergo thermal dehydration and ring closure to the corresponding cyclic imidazoline derivative.



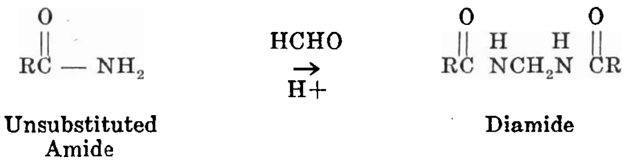
$$R\overset{\overset{O}{\|}}{C}OH + H_2NCH_2CH_2\overset{H}{N}CH_2CH_2NH_2 \rightarrow R\overset{\overset{O}{\|}}{C}-\overset{H}{N}CH_2CH_2\overset{H}{N}CH_2CH_2NH_2$$

Diethylene Triamine

"Imidazoline"

These are finding application as asphalt anti-stripping additives, as emulsifiers (cationic), in ore flotation, and as intermediates in quaternary ammonium salt formation.

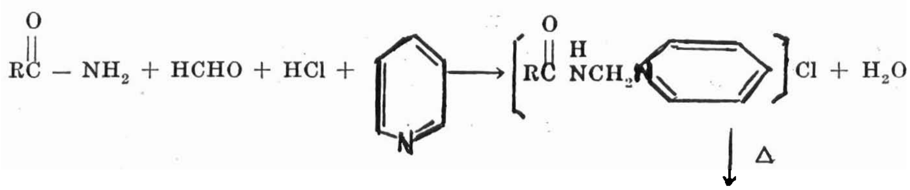
The simplest of the amides, and most promising from a chemical intermediate standpoint, are those derived from fatty acids and ammonia. Under the proper conditions, about 200°C. under a slightly vented ammonia atmosphere, the intermediate ammonium soap decomposes, loses a mol of water and is converted to the unsubstituted amide. These are, generally, neutral, waxy, high-melting solids, of low water solubility. They are useful, in themselves, as anti-tack and anti-blocking agents, as foam boosters and stabilizers for the synthetic anionic detergents, as mutual solvents for blending waxes and plastics, as ink additives, etc. One of their largest uses, however, depends upon further reaction with formaldehyde. Alone, with an acid catalyst, the diamides are formed, potential wax extenders and substitutes.



$$R\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[H+]{HCHO} R\overset{\overset{O}{\|}}{C}\,\overset{H}{N}CH_2\overset{H}{N}\,\overset{\overset{O}{\|}}{C}R$$

Unsubstituted Amide Diamide

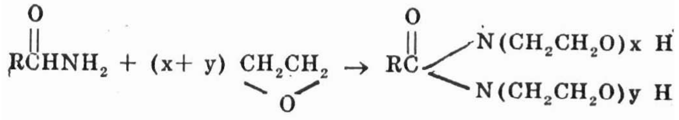
In conjunction with pyridine and HCl, the resulting quaternary is a fabric softener and water repellent.



Water Repellent Film

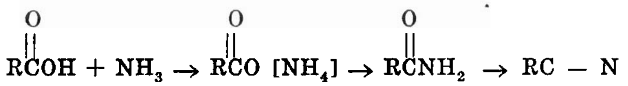
Applied in solution and decomposed by heat, the so-called Zelan process, a water repellent film deposits on the fabric.

Reaction with ethylene oxide gives a series of water dispersible or soluble products, useful as dispersing agents, in waterless hand cleaners, in buffing sticks and liquids and as silicone and wax emulsifiers.



Ethylene Oxide "Ethomid"®

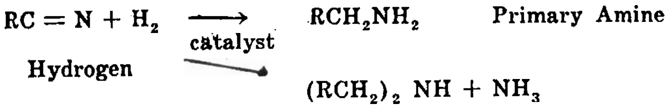
However, the most versatile outlet for the unsubstituted amides is as their decomposition products, the nitriles. These are formed by the loss of a mol of water from the amide, under essentially vapor-phase, catalytic, dehydration conditions.



$$R\overset{O}{\overset{\|}{C}}OH + NH_3 \rightarrow R\overset{O}{\overset{\|}{C}}O\,[NH_4] \rightarrow R\overset{O}{\overset{\|}{C}}NH_2 \rightarrow RC - N$$

Ammonia Soap Amide Nitrile

Their uses, per se, are limited, as plasticizers and yarn spinning lubricants. Their most important reaction, however, is reduction to the primary or symmetrical secondary amines, source materials for a score of versatile and interesting derivatives.



$$RC = N + H_2 \xrightarrow{\text{catalyst}} RCH_2NH_2 \qquad \text{Primary Amine}$$

$$\searrow (RCH_2)_2\ NH + NH_3$$

Hydrogen

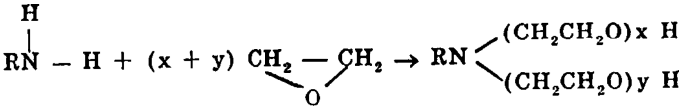
Secondary Amine

These amines are prepared under catalytic hydrogenation conditions, under hydrogen pressure and using Raney Ni as the catalyst. Choice of reaction conditions, particularly temperature, will determine the direction of reduction. Low temperatures give the primary amines; higher temperatures the scondary amines. Both are considered as substituted ammonias.

The primary amines are weak bases, easily neutralized by organic or inorganic acids and ionizing, as such or as their salts, as cationic agents. The salts are essentially water soluble and exhibit marked surface activity. As such, and because of their tendency to be adsorbed on charged surfaces, they have found wide outlets in industrial applications. The first successful use for these compounds was in the ore flotation field in the selective adsorption on and separation of one component from another in a non-metallic mixture. The separation of KC1 from NaC1, in a naturally occurring blend, is a good example of the specific activity of these compounds. They are used, too, as rust and corrosion inhibitors, as emulsifiers and surface-active agents for degreasers, in drawing compounds, as anti-stripping agents in asphalt mixtures, as fungicides and germicides, as mold release agents in butyl rubber compounding, as pigment dispersing agents, in lubricating and cutting oils, in caulking compounds, in metal cleaners, etc.

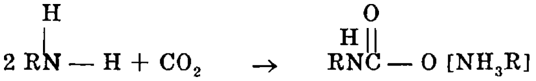
The secondary amines, although slightly more basic than the primary amines, have many characteristics in common with them. They are surface-active, cationic materials, which, however, give rise to hydrocarbon-soluble salts on acidification, with obvious application advantages. Although only recently available compounds, their potential markets are quite substantial.

In terms of strictly chemical approaches to the amines, many avenues of derivative rsearch and reaction are available. Some have already successfully reached volume production. The amines, since they contain active hydrogen atoms, will undergo reaction with ethylene oxide, giving rise to a series of basic, cationic derivatives containing the derived ethoxy units in the molecule.



"Ethomeen"®

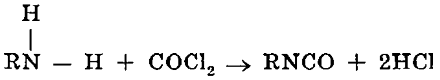
They are useful as emulsifying agents, in soluble cutting oils, as anti-static agents, in dry-cleaning detergents, etc. The amines will form carbamates with CO_2, an easily reversible reaction;



$$2\,R\overset{H}{\overset{|}{N}} - H + CO_2 \rightarrow R\overset{H}{N}\overset{O}{\overset{\|}{C}} - O\,[NH_3R]$$

Carbon Dioxide Carbamate

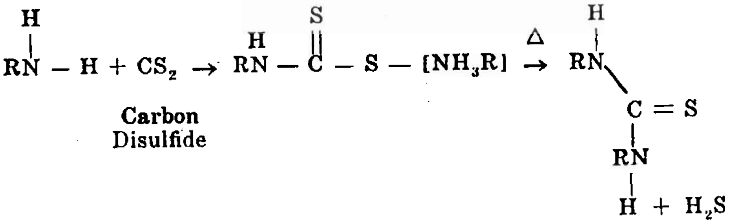
they can be converted to the isocyanates, useful as toxicants, with phosgene;



$$R\overset{H}{\overset{|}{N}} - H + COCl_2 \rightarrow RNCO + 2HCl$$

Phosgene Isocyanate

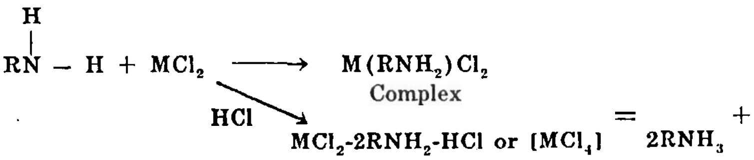
they will form dithiocarbamates or substituted thioureas with carbon disulphide;



Carbon Disulfide

Thiourea

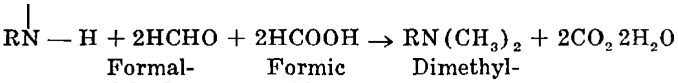
they will form complexes or double salts with inorganic heavy metal salts, useful as agricultural chemicals and mold inhibitors;



Complex

Double Salt

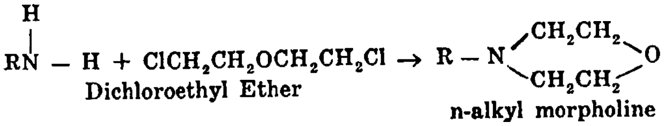
they will give the tertiary amines (intermediates in quaternary formation) with formic acid and formaldehyde;



$$R\overset{H}{\overset{|}{N}} - H + 2HCHO + 2HCOOH \rightarrow RN(CH_3)_2 + 2CO_2\,2H_2O$$

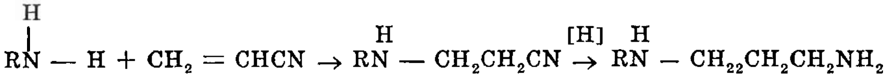
Formaldehyde Formic acid Dimethylamine

they will form substituted morpholines;


Dichloroethyl Ether

n-alkyl morpholine

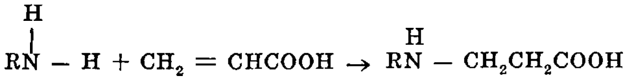
they will react with acrylonitrile and give, on reduction, a versatile polyamine containing a primary and secondary amine grouping (useful as a corrosion inhibitor and asphalt additive);


$$R\overset{H}{N} - H + CH_2 = CHCN \rightarrow R\overset{H}{N} - CH_2CH_2CN \xrightarrow{[H]} R\overset{H}{N} - CH_{22}CH_2CH_2NH_2$$

Acrylonitrile

Diamine

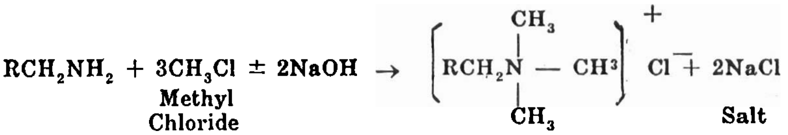
and they will react with acrylates and crotonates to give alkyl substituted amino acids, or Zwitterions, valuable detergents and surface-active agents.


$$R\overset{H}{N} - H + CH_2 = CHCOOH \rightarrow R\overset{H}{N} - CH_2CH_2COOH$$

Acrylic Acid

Amino Acid

However, the largest class of amine derivatives is that encompassing the quaternary ammonium compounds. These are prepared by the exhaustive alkylation of the amines, giving a positively charged long chain as the cation and containing a pentavalent nitrogen atom with four co-valent carbon substituents and an electrovalent-bonded anion. These compounds are extremely valuable surface-active agents, and are obviously capable of great structural variation. The primary and secondary amines are alkylated with methyl chloride, dimethyl sulfate, etc., in solvent and in the presence of an inorganic alkali;

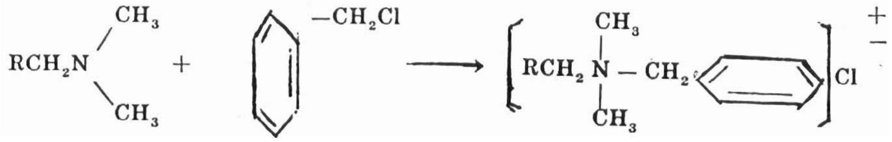

$$RCH_2NH_2 + 3CH_3Cl \pm 2NaOH \rightarrow \left[RCH_2\overset{CH_3}{\underset{CH_3}{N}} - CH^3 \right]^{+} Cl^{-} + 2NaCl$$

Methyl Chloride

Quaternary Ammonium Chloride

Salt

Tertiary amines react directly with the alkylating agent.


n,n-Dimethyl Alkylamine

Benzyl Chloride

These salts, and they are true ionizable salts, are usually water soluble, although those derived from the symmetrical secondary amines, again, are hydrocarbon soluble.

The very high germicidal and fungicidal activity of the quaternary amonium salts was noted fairly early in their development, and extensive investigations of this applied phase have been undertaken. They are being used now in the food industry, as sanitizing agents and equipment cleaners, as sterilizers for surgical instruments and in wound control; they are finding outlets in the secondary oil recovery field (those derived from the secondary amines are oil-soluble) as inhibitors for sulfate-reducing organisms; they are used as wetting and finishing agents in the textile industry; as anti-static agents in the plastic and fiber industries; as after-rinses in laundry washing, for their germicidal and very noticeable cloth-softening effects; as flotation agents; as ingredients in Bentone grease formulations — particularly the di long-alkyl-chain derivatives; etc. On the debit side they are not particularly good detergents themselves and are incompatible with anionics. Their advantages far outweigh their disadvantages, however.

In general, the nitrogen-containing fatty-acid-derivatives field is a promising one. Its fundamental assets are the surface activity of its members, tailor-made by varying the molecular elements; its many avenues for derivative variation, its chemical versatility and functional group variability; and a potentially cheap and plentiful source of supply.

STORAGE AND HANDLING OF FATTY ACIDS

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In discussing this subject, let me very briefly outline the nature, source, and methods of producing fatty acids. Fats and oils, whether from animal, vegetable, or marine origin, when hydrolyzed, yield crude fatty acids and crude glycerine which are then further purified.

Fatty acids may be subdivided into two main groups — saturated and unsaturated. Both these groups exist in the liquid and solid state, depending on their purity. Commercially available grades of fatty acids are being produced in the folowing types:

Crude — Distilled — Fractionated — Solvent Separated — Bleached.

In the manufacture of distilled and/or fractionated fatty acids, great care is exercised to produce fatty acids of the highest purity. By this I mean fatty acids free of gummy materials, unsaponifiables, etc., and — last but not least — free of metallic impurities, such as copper and iron, which are the most common contaminants affecting color and stability towards rancidity of fatty acids.

Unsaturated fatty acids — such as oleic, linoleic and linolenic — are by far the most sensitive to oxidation. Since almost all fats and oils contain some percentage of these unsaturates, they are thus subject to oxidative rancidity.

In the handling of fatty acids, therefore, it has become necessary to preserve quality from start to finish. Mainly, the equipment used during manufacture should be of such material as to minimize, if not entirely eliminate, the possibility of metallic contamination, and air oxidation. Present day engineering, coupled with chemical technology, has made available such materials of construction to the fatty acid manufacturer and the user. Materials most commonly used are stainless steel type 316, aluminum, glass, rubber, acid-resistant tile, phenolic, or epon lined steel. These are just a few of the construction materials available today.

The trend in the fatty acid consuming industry today is more and more toward bulk handling of this commodity. Consumers of fatty acids have begun to realize the importance of savings effected by eliminating, as far as possible, drum or small package shipments and use. You save not only when you buy the acids, but also in the handling and use of these acids in your plant and in processing. In addition, labor and time saving are factors not to be overlooked; also transportation costs have gone up tremendously.

Fatty acids can be and are being shipped in tank cars or tank wagons, in standard sizes. These come in aluminum, glass-lined, phenolic or epon-lined, stainless steel, or *regular steel* — although, in this day and age, I cannot conceive of any fatty acid manufacturer, after spending money to distill fatty acids, shipping in an ordinary steel tankcar nor the consumer accepting such shipments regardless of the type of fatty acid being shipped or to what use it is to be put.

For bulk handling of fatty acids, whether inside or outside installation, it is necessary to provide heating coils for steam or hot water when available. In our plant, we like the idea of putting these heating coils underneath the tanks and not inside. We like this system because, in changing from stock to stock, it eliminates costly cleaning, and there is also greater ease in what cleaning must be done. Also, when steam is being used in place of hot water, there is no danger of overheating, and the coils do not have to be of stainless steel or aluminum; ordinary steel will suffice.

Another very important point in bulk handling is that you can provide an atmosphere of nitrogen over the fatty acid, by bubbling nitrogen from a bottle in the storage tank to retard air oxidation and thus delay discoloration. This also serves to keep contents from stratification.

If help is needed in the installation of fatty acid storage tanks, and handling equipment in your plant, consult your fatty acid supplier for engineering and technical assistance. I am sure he is well equipped to provide the necessary help and know-how.

If you are now using an ordinary steel tank for handling fatty acids, I believe it is about time you either changed to a non-corrosive tank or had your tank lined with baked-on phenolic resin coating. There are a number of well known houses equipped to do this work either on your own premises or at their factory.

In handling liquid or semi-liquid fatty acids in smaller containers, such as 55-gallon drums or smaller, epoxy resin finishes are preferred, because such linings approach the excellent chemical resistance of the brittle pure phenolic linings, and are at the same time quite flexible and resistant to reverse impact, that is, they show no chipping or fracture when dropped or hit by another drum or object.

There are, of course, now in commercial use, aluminum and stainless steel drums, and while these must still be used for some acids, the main objections to them are the heavy deposit that one must make in addition to the added cost of returning them.

For more detailed information on materials of construction and method of handling now in use, may I suggest you get a copy of the publication prepared by the Fatty Acid Division of the Association of American Soap and Glycerine Producers, Inc., by writing your fatty acid supplier. The title of this publication is, "HOW TO HANDLE FATTY ACIDS IN SHIPMENT — IN STORAGE IN USE."

APPLICATIONS FOR FATTY ACIDS

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Delivered by R. D. AYLESWORTH

I. FATTY ACIDS FOR METALLIC SOAPS

INTRODUCTION

The purpose of this paper is to review briefly the commercially fatty acids used in the manufacture of metallic soaps. Elliott[3] defines metallic soaps as the alkali, alkaline-earth, or heavy-metal salts of monobasic, complex organic salts. The more commonly accepted industrial connotation excludes the water soluble sodium and potassium soaps. Tallates, resinates, and naphthenates are not considered in this presentation.

LITERATURE

Any reasonably complete summary of references to the use of fatty acids for metallic soaps is beyond the scope of this paper. However, the listing of several general sources of information may be of value to technical personnel who are not intimately acquainted with the field.

Elliott's American Chemical Society monograph *The Alkaline-Earth and Heavy-Metal Soaps*[3] affords a standard textbook treatment of metallic soaps. The Texas Company has published a compilation of *Properties of the Principal Fats, Fatty Oils, Waxes, and Fatty Acids and Their Salts*[2] including a bibliography of more than 600 references. Wendt and Wagner[5] have provided a summary of manufacturing procedures and end-uses for metallic soaps. Licata[4] has related fatty acid composition and the common manufacturing procedures for metallic soaps. An excellent summary of lubricating grease applications for metallic soaps may be found in Boner's *Manufacture and Application of Lubricating Greases.*[1]

One important source of information relative to metallic soaps might be overlooked: the manufacturers of metallic soaps. The industry stresses application research to a high degree. Most manufacturers of metallic soaps have well-qualified technical personnel who specialize in application research and are available for discussion of specific application problems.

MAJOR FATTY ACID PRODUCTS USED FOR METALLIC SOAPS

In various degrees of purity or grade, the following fatty acid products account for the major volume of sales to manufacturers of metallic soaps:

Stearic acid
Hydrogenated Tallow acids
Hydrogenated Fish acids
Oleic acid
Vegetable Faty acids (high iodine value)
Coconut acids

TABLE I

Composition of Major Commercial Fatty Acids Used in the Manufacture of Metallic Soaps

Commercial Product	Saturated Acid Composition	Unsaturated Acids
Stearic Acid	91-99.5% (55 parts C_{16}) (45 parts C_{18})	0.5-9%
Hydrogenated Tallow Fatty Acids	91-99.5% (70 parts C_{18}) (30 parts C_{16})	0.5-9%
Hydrogenated Fish Acids	95-99% (mixture C_{16}-C_{22})	1-5%
Oleic Acid	5-10% (C_{14}-C_{16})	90-95%
Vegetable Fatty Acids	5-30% (C_{16}-C_{18})	70-95%
Coconut Acids	90-99% (mixture C_8-C_{18})	1-10%

Table I is a summary of the compositions of the major commercial fatty acids used in the manufacture of metallic soaps. Of the individual component fatty acids found in these products eight account for an overwhelmingly large proportion of the total fatty acid usage by metallic soap producers. These are stearic (C_{18} saturated), palmitic (C_{16} saturated), arachidic (C_{20} saturated), behenic (C_{22} saturated), lauric (C_{12} saturated), oleic (C_{18} monounsaturated), linoleic (C_{18} diunsaturated), and linolenic (C_{18} triunsaturated).

SPECIALTY FATTY PRODUCTS USED FOR METALLIC SOAPS

Table II is a listing of a number of specialty fatty acid and fatty derived products used for manufacture of metallic soaps. Some of these specialty products are used as modifiers for standard metallic soaps. Others are used as the total organic components. All offer the manufacturer of metallic soaps and his customers the opportunity of attaining optimum answers to specific industrial requirements.

TABLE II

Specialty Fatty Acid and Fatty Derived Products Used in the Manufacture of Metallic Soaps

Commercial Designation	Chemical Characterization
Caprylic Acid	C_8 Saturated Acid (90-95% purity available)
Pelargonic Acid	C_9 Saturated Acid (90+% purity available)
Capric Acid	C_{10} Saturated Acid (90-95% purity available)
Lauric Acid	C_{12} Saturated Acid (90-95% purity available)
Myristic Acid	C_{14} Saturated Acid (90-95% purity available)
Palmitic Acid	C_{16} Saturated Acid (70-90% purity available)
Stearic Acid	C_{18} Saturated Acid (80-95% purity available)
Modified Fatty Acids	60-70% C_{16}-C_{18} Saturated + 30-40% Unsaturated Acids
Low Linoleic Oleic Acid	C_{18} Mono unsaturated acid with a low poly unsaturated acids content
Ricinoleic Acid	Liquid Monohydroxyoleic acid derived from castor oil
12-Hydroxystearic Acid	Hydrogenated Ricinoleic Acid
Azelaic Acid	C_9 Dicarboxylic Acid
Sebacic Acid	C_{10} Dicarboxylic Acid
Dimer Acid	C_{36} Dicarboxylic Acid

APPLICATIONS FOR METALLIC SOAPS

Typical applications for metallic soaps of several fatty acids are indicated in Table III. The number of commercially available metallic soaps of fatty acids is, of course, much larger. Obviously, the potential number that could be produced by different methods of manufacture from various combinations of the scores of commercial fatty acids and 40-45 readily available metals is astronomical.

TABLE III

Typical Applications for Several Metallic Soaps of Fatty Acids

Fatty Acid	Metal	Typical Application
Stearic Acid	Calcium	Cosmetic Formulation
Hydrogenated Tallow Acids	Zinc	Rubber Compounding
Hydrogenated Fish Acids	Aluminum	Flattening Agent
Oleic Acid	Copper	Mildew Prevention
Vegetable Acids	Manganese	Paint Drier
Lauric Acid	Cadmium-Barium	Vinyl Stabilizer
12-Hydroxystearic Acid	Lithium	Lubricating Greases

CONCLUSIONS AND SUMMARY

The major sales volume of fatty acids to producers of metallic soaps is accounted for by a restricted group of products and component acids. There are, however, many additional fatty acid and fatty derived products that meet special requirements of the metallic soap industry.

Tremendous technological progress during the past two decades has been a characteristic of the fatty acid industry. The primary benefits to manufacturers of metallic soaps and their customers have been threefold (1) standardization of commodity fatty acids (2) availability of fatty acids of higher purity, and (3) development of new and unique fatty acid and fatty derived chemicals.

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J. Am. Oil Chemists Soc., 31, 590 (1954),
Applications of Fatty Acids in Metallic Soaps

II. INFLUENCE OF FATTY ACID COMPOSITION ON VISCOSITY OF POTASH LIQUID SOAPS

Potash liquid or paste soaps are available commercially in concentrations ranging from 10 per cent to 80 per cent. Potash soaps are characterized by good detergency, ready solubility and rinsibility, clarity at low temperature, mild odor, and excellent lubricity. Important sales outlets include liquid hand soaps, scrub soaps, and various lubricant applications.

The primary objective of this presentation is to report data showing the influence of saturated fatty acids of varying chain length on the viscosity of potash liquid soaps of oleic acid. Although this paper is restricted to modification of the potash soap of oleic acid, the general principles established are applicable to potash soaps of a broad range of fatty products.

HISTORICAL

Viscosity is one of the most important characteristics of liquid soaps. However, comparatively little information relating to the influence of fatty acid composition on liquid soap viscosity is available in the literature. Mikumo[3] has concluded that highly soluble lower molecular weight fatty acids have a significant influence on the solubility of stearate soaps. Behrmann[1] has reviewed the subject of liquid soaps and presented some maximum soap concentrations for liquid potash soaps of several commercial fatty acids. Behrmann has also pointed out the importance of unsaponifiable content and state of oxidation of the fatty components on the viscosity of potash liquid soaps. Spencer[4] has reported viscosity data for potassium soap-potassium silicate mixtures.

Feldpush and Sutker[2] have made a detailed study of composition factors influencing the viscosity of liquid potash soap of a typical soya fatty acid. The effects of variations in stearic, palmitic, oleic, linoleic, and linolenic acids and unsaponifiable content have been included in this report. It has been concluded that "the composition of fatty acids and the concentration of unsaponifiable are definitely variables which do affect the clarity and viscosity of 20 per cent potash soap solutions."

Trusler[5] has studied the viscosities of coconut oil liquid soaps. The influence of temperature and soap concentration on viscosity is covered in this reference. Viscosity differences between liquid potash soaps of coconut oil vs. coconut fatty acids are reported.

EXPERIMENTAL

Viscosities of solutions of neutral potash soaps in distilled water were measured at concentrations ranging from a lower level of 5-15 per cent soap content (five to ten centipoises) up to the concentrations giving a viscous liquid (150-250 centipoises). All viscosities were determined at 25 ± 0.2°C. The liquid soaps studied were based on oleic acid and oleic acid modified with various proportions of saturated fatty acids. Viscosities were obtained with a Brookfield Viscosimeter (Model LVF) which is described by Trusler.[5]

The following fatty acids were employed in this study:

1. Oleic Acid — A low linoleic oleic acid. The potash liquid soaps of different production lots of this type of commercial oleic acid are remarkably uniform in viscosity characteristics. Furthermore, viscosity-concentration relationships for this potash soap are in the same general range as potash soaps of other commonly used oleic and vegetable fatty acids. In contrast, it has been demonstrated (unpublished work, Emery Industries, Inc.) that the potash soap of highly purified oleic acid gels at a much lower soap concentration than the potash soaps of commercial low titre fatty acids.
2. *Stearic Acid* — Iodine Value: less than 0.5; C_{18} saturated acid content: 87 per cent.
3. *Palmitic Acid* — Iodine Value: less than 2.0; C_{16} saturated acid content: 90 per cent.
4. *Myristic Acid* — Iodine Value: less than 1.0; C_{14} saturated acid content: 94 per cent.
5. *Lauric Acid* — C_{12} saturated acid content: 95 per cent.
6. *Capric Acid* — C_{10} saturated acid content: 92 per cent.
7. *Pelargonic Acid*—C_9 saturated acid content: 91 per cent.
8. *Caprylic Acid* — C_8 saturated acid content: 93 per cent.

Potash soaps of oleic acid and oleic acid modified with varying proportions of each of the saturated acids were prepared at soap concentrations sufficiently high that thick, viscous liquids were obtained at 25°C. The requisite amount of reagent grade of caustic potash was dissolved in distilled water and heated to 65-70°C. The appropriate quantity of fatty acid, heated separately to 65-70°C, was added in a steady stream to the caustic solution with vigorous agitation. Agitation was continued until a uniform solution was obtained. The soap solutions were checked for neutrality in boiling neutral isopropyl alcohol containing phenolphthalein. Neutrality was assumed when the alcohol turned a very faint pink on addition of soap.

After preparation, the soap solutions were allowed to stand over night. The temperature was then adjusted to 25 ± 0.2°C. After an initial viscosity reading the liquid soaps were diluted with increments of water so that the soap concentration was reduced 0.5 per cent per water addition. The liquid soap was stirred thoroughly after each water addition, checked for temperature, and the viscosity again measured. Soap concentration intervals were extended as soon as the viscosity changes became minor.

RESULTS

Experimental liquid soap viscosity data are presented in Table IV and V and Graphs A and B.

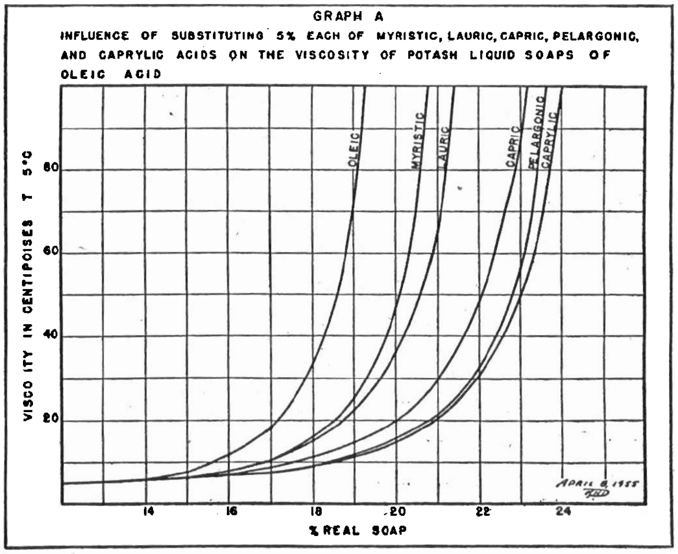
TABLE IV

Influence of Substituting Stearic and Palmitic Acids on the Viscosity of Potash Liquid Soaps of Oleic Acid

Potash Soap of	Viscosity in Centipoises at 25°C. 17% Real Soap	 18% Real Soap	 19% Real Soap
Oleic Acid	18.4	33.4	70.8
97½% Oleic—2½% Stearic	18.5	33.5	83.6
95% Oleic— 5% Stearic	16.5	29.5	67.5
90% Oleic—10% Stearic	16.6	29.7	67.5
80% Oleic—20% Stearic	17.6	35.9	83.4
97½% Oleic—2½% Palmitic	16.2	28.1	60.0
95% Oleic— 5% Palmitic	16.2	27.2	58.9
90% Oleic—10% Palmitic	16.0	27.2	60.5
80% Oleic—20% Palmitic	16.5	31.2	59.5

Table IV is a summary of viscosity data for 17, 18, and 19 per cent potash liquid soaps of oleic acid and oleic acid modified with 2½, 5, 10 and 20 per cent palmitic or stearic acid.

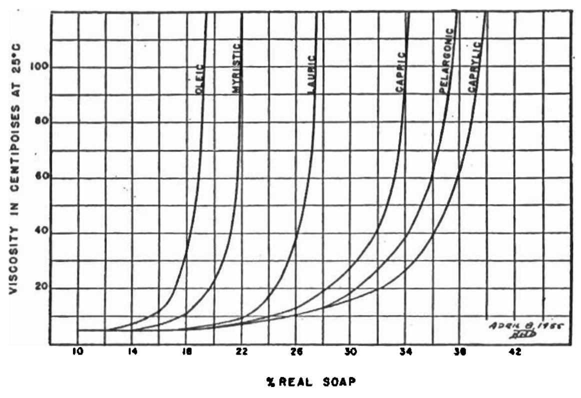
Graphs A and B demonstrate the influence of substituting 5 per cent and 20 per cent each of C_{14} (myristic), C_{12} (lauric), C_{10} (capric), C_9 (Pelargonic), and C_8 (caprylic) acids for oleic in potassium oleate liquid soap.


GRAPH A

INFLUENCE OF SUBSTITUTING 5% EACH OF MYRISTIC, LAURIC, CAPRIC, PELARGONIC, AND CAPRYLIC ACIDS ON THE VISCOSITY OF POTASH LIQUID SOAPS OF OLEIC ACID

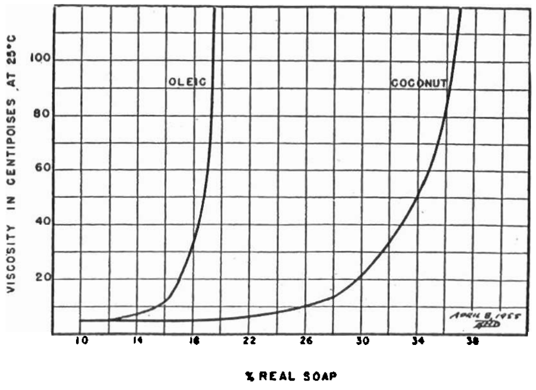
GRAPH B

INFLUENCE OF SUBSTITUTING 20% EACH OF MYRISTIC, LAURIC, CAPRIC, PELARGONIC, AND CAPRYLIC ACIDS ON THE VISCOSITY OF POTASH LIQUID SOAPS OF OLEIC ACID



GRAPH C

VISCOSITY-CONCENTRATION RELATIONSHIPS OF THE POTASH LIQUID SOAPS OF COMMERCIAL OLEIC ACID AND COCONUT FATTY ACIDS



The effect on liquid soap viscosity of 2½, 5, 10 and 20 per cent modification of potassium oleate solutions with saturated acids is shown in Table V. Concentrations of the various soaps required to achieve viscosities of 20 centipoises and 80 centipoises at 25°C. are given. The data for Table V were derived by determining soap concentration-viscosity relationships at 25°C. for potash liquid soaps of oleic acid and oleic acid modified with varying proportions of saturated acids. The liquid soap concentrations exhibiting viscosities of 20 centipoises and 80 centipoises were obtained from the individual viscosity-soap concentration curves.

TABLE V

Real Soap Concentrations for Potassium Oleate Soaps Exhibiting Viscosities of 20 Centipoises and 80 Centipoises at 25° C. When 2½%-20% Saturated Fatty Acids Are Substituted for Oleic Acid

% Modifying Acid Content	% Real Soap Exhibiting 20 Centipoises 2½	5	10	20	% Real Soap Exhibiting 80 Centipoises 2½	5	10	20
Modifying Fatty Acid								
Stearic	17.1	17.4	17.2	17.2	19.0	19.2	19.1	19.0
Palmitic	17.4	17.4	17.5	17.2	19.4	19.4	19.4	19.3
Myristic	17.7	18.6	18.6	19.8	19.7	20.6	20.6	21.8
Lauric	17.8	18.7	19.9	24.5	20.0	21.2	23.5	27.5
Capric	18.4	20.0	23.7	28.4	21.1	22.9	27.0	31.6
Pelargonic	18.6	20.8	26.2	30.5	21.2	23.4	29.1	36.8
Caprylic	18.9	20.9	26.3	32.1	21.3	23.8	31.9	38.8

17.0% Potassium Oleate Solution has a viscosity of 20 Centipoises

19.1% Potassium Oleate Solution has a viscosity of 80 Centipoises

DISCUSSION

Among the commercially available fatty acids, oleic acid, soya acids, corn acids, other high iodine value vegetable fatty acids, and coconut fatty acids are commonly used for potash liquid soaps. Graph C shows the viscosity-soap concentration relationships at 25°C. for potash liquid soaps of a commercial coconut fatty acid vs. a commercial grade of oleic acid. Curves similar to the oleic soap solutions are obtained from potash liquid soaps of soya acids, corn acids, tallow acids, and other C_{16}-C_{18} fatty acids is in the range of 18-22 per cent soap concentration.[1] The level will vary somewhat depending on fatty acid composition, unsaponifiable content, and state of oxidation.[1,2] That saponification number, titre, iodine value, etc., are of limited value in predicting viscosities of liquid soap solutions is demonstrated by the data in Table VI.

Coconut fatty acids are unique among the commonly available commercial fatty acids in allowing preparation of a 35-36 per cent free-flowing potash soap.[5] The less frequently used babassu and palm kernel fatty acids are, of course, similar in composition to coconut acids and high concentration liquid soaps can be prepared from these as well as from coconut.

From the data in Tables IV and V it is concluded that substitution of up to 20 per cent C_{16} — C_{18} saturated fatty acids for oleic acid has comparatively little influence on the potash liquid soaps of fatty acids containing high proportions of stearic and palmitic acids are unsatisfactory for many applications because of poor cold test.[2]

C_{14} and lower molecular weight fatty acids have a pronounced effect in reducing the viscosity of potasium oleate liquid soap. Pelargonic and caprylic are particularly effective as can be seen from Graphs A and B and Table VI.

TABLE VI

Analytical Data and Potash Liquid Soap Viscosities For Two Oleic Acids and Two Soya Fatty Acids

	Oleic A	Oleic B	Soya A	Soya B
Iodine Value	92.5	89.7	124.0	119.6
% FFA (as Oleic)	100.0	100.8	101.0	101.5
Saponification No.	200	202	202	203
% Unsaponifiable	1.2	2.2	.5	1.3
Titre °C.	8.7	9.7	27.7	26.2

22% Potash Soap Solution at 25° C.

Viscosity (Centipoises)	450	8.5	18,800	9.6

It is evident from examination of the experimental data that substantial viscosity modification of potash liquid soaps of oleic acid can be accomplished by addition of relatively small proportions of low molecular weight fatty acids. A liquid soap that is equivalent in viscosity characteristics to potash liquid coconut soap can be prepared from a blend of oleic acid (or mixed C_{16}-C_{18} vegetable acids and 15-20 per cent of caprylic or pelargonic acid.

Viscosity is only one of the important characteristics of potash liquid soaps. Sudsing is particularly important in the case of liquid hand soaps. Sudsing of potash soaps of oleic and low molecular weight acid mixtures is not equivalent to the sudsing of the potash coconut soaps commonly used for liquid hand soaps. However, sudsing of soaps of combinations of coconut and oleic mixtures is entirely satisfactory for many applications including liquid hand soaps.

The commercial significance of such blends can be appreciated from consideration of the folowing factors relative to coconut oil (1) coconut is an imported oil subject to the vagaries of international trade, war, and defense priorities, (2) coconut oil prices are dictated by world price levels for edible oils in contrast to the prices of fatty acids derived from inedible oils and fats, (3) coconut oil is subject to a tariff of 3¢ per pound when used for soap making in the United States.

Blends of oleic and the low molecular weight acids, caprylic, pelargonic, and capric, are frequently attractive cost-wise in comparison to coconut oil or coconut fatty acids. Caprylic and capric acids are obtained industrially from fractionation of coconut. The acids are by-products in the production of topped coconut acids or high purity lauric acid. Pelargonic acid is derived from oxidation of oleic acid which, in turn, is derived from inedible tallow.

SUMMARY

Experimental data are reported to show the influence of substituting up to 20 per cent saturated fatty acids of varying chain lengths for oleic acid in potassium oleate liquid soaps. It is concluded that stearic and palmitic have only a minor influence on the viscosity of potassium oleate liquid soaps at 25°C. Significant reduction in viscosity of potassium oleate solutions is realized by substituting myristic, lauric, capric, pelargonic, and caprylic acids for oleic. Pelargonic and caprylic are particularly effective. A product equivalent in viscosity characteristics to liquid potash coconut soap can be prepared from a blend of oleic acid (or mixed C_{16}-C_{18} vegetable acids) and 15-20 per cent caprylic or pelargonic acid.

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FATS AND OILS IN THE AUTOMOTIVE CHEMICAL AND INDUSTRIAL CHEMICAL MAINTENANCE FIELD

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In our part of the symposium, we will not attempt to discuss the technical aspects of fats and oils and their use in compounding finished products, as we feel this will be discussed by other speakers. We will attempt to show you the important role that these intermediates play in industry today.

Animal and vegetable fatty acids and oils as intermediates have great importance in the formulation of automotive chemicals, industrial maintenance chemicals, and sanitary chemicals. Some of the major products in this field, using these fats and oils are: hydraulic brake fluids, rubber parts lubricants, special automobile lubricants, leather finishings, disinfectants, floor cleaners, floor polishes, paint removers, airplane cleaners, and many other items.

To manufacture these products the major fats and oils used are: red oil (both crude and refined), tall oil, coconut oil, coconut fatty acid, corn fatty acid, cotton seed fatty acid, lard oil, mixed vegetable fatty acids and oils, wood rosin and castor oil. There are many refined straight chain fatty acids with a controlled carbon length for special purposes and for specific uses.

It will be noted as the various products using the fats and oils are described, there is a trend towards, in some cases; and away, in other cases, from these ingredients. New intermediates are replacing old compounds, and in turn old intermediates are being replaced when new uses of fats and oils are discovered. Hydraulic brake fluids consume a major proportion of castor oil used in this country. Castor oil for this product seems to have the proper viscosity, the proper freezing point, and has a minimum change in its chemical constituency when the fluids reach the boiling point. These hydraulic brake fluids contain approximately 10 per cent to 20 per cent of castor oil. It is estimated that approximately 4,500,000 lbs. of castor oil are used annually in these fluids.

In recent years there has been a gradual trend away from castor oil bases in these hydraulic fluids, towards what is known as synthetics which are made primarily of glycols. From this trend, we assume that castor oil has reached its peak for this use and a decline will take place over a period of years.

Rubber lubricants have found a new use with the advent of tubeless tires, and have been rejuvenated in the automobile industry. Castor oil will be the oil base for these lubricants. One of the real advantages of castor oil in this type of lubricant is that when the lubricant is properly formulated, excellent lubricity results without causing undue deterioration of the rubber. However, when the solvents have evaporated, these compounds become sticky and tacky, giving us good adherent properties for these tubeless tires on the rim of the automobile. We feel that these rubber lubricants will replace the loss that there may be from the trend away from castor oil in hydraulic brake fluids.

The penetrating oils and other special automotive lubricants have saponified animal and vegetable fatty acids and oils. These lubricants are built for special duties to aid in the operation of the automobile, and I have been told that their viscosity, stability, and lubricity can be easily controlled by making soaps from known fatty acids and fatty oils.

One of the earliest uses of soap, for other than household use, was in leather finishings, the popular product being saddle soap. Modifications of saddle soap are still being used in finishing, cleaning, buffing, and softening of tanned leather goods. Originally, saddle soap was made from animal fats and oils. However, recently, the trend has been towards vegetable fats and oils.

The basic solvent and emulsifier for coal tar, pine oil, cresylic acid, chlorinated phenol, and similar type disinfectants are made from soap. The better the disinfectant, the better the quality of soap. Rosin oils are used along with other fats and oils for the manufacture of these sanitary products. Most disinfectants contain 10 per cent anhydrous soap, and in stipulating the quality of disinfectants many specifications insist on this quantity of soap.

Two of the larger volume products using soaps made from fatty acids and oils are industrial floor cleaners and floor polishes. It has been found that soap is necessary in most floor cleaners. Many of these cleaners today contain detergents such as the phosphates, synthetics, etc., but it seems that to get good dirt removability and good foam control it has been necessary to add anhydrous soaps. In emulsion floor waxes and polishes, the emulsifiers are amine soaps. So much is thought of the fatty acid used in these soaps that control of the quality floor finishing compound can be governed by the type of fatty acid or oil used.

The aviation industry, along with the automotive industry, uses considerable volumes of specially blended soaps. These soaps are used in addition to general cleaning compounds, degreasing, and general removal of petroleum staining and carbon removal ability. This type of product is usually diluted in petroleum distillates of a kerosene type, slushed over the equipment to be cleaned, allowed to penetrate a short time, scrubbed, and then flushed with water. The soap immediately emulsifies into the water and is rinsed away. The U. S. Air Force used approximately 5,000,000 gallons of such a soap last year which is equivalent to 40,000,000 lbs. of anhydrous soap.

Among the miscellaneous products, one item that is gradually becoming very important is the paint remover. Paint removers are usually made of strong alkalies with chlorinated solvents. Again it was found that to slush away the removed paint, along with the paint remover, it was necessary to incorporate soaps into the product.

Fatty acids and oils among our populace are thought of only in the term of household soaps and cleansers. Those of us in the Industrial Chemical field dispute this, because it can be seen from the foregoing outline that true soap is a necessary chemical intermediate for the compounding of many of our maintenance products. For years the chemist has attempted to replace these saponified products with the so-called synthetics, and invariably he has reverted to soap. Along with many of our other chemical compounds, animal and vegetable fatty acids have a very important place in the formulation of useable chemical products.

PANEL DISCUSSION

Mr. Terry: If there are no more questions to be turned in, we will proceed with the question and answer period. If there are any additional thoughts from the audience please do not hesitate to raise any questions and we will recognize you. Also, as I mentioned earlier, I would like to have the panel members ask each other questions if they so desire.

The first question is directed to Mr. Aylesworth. It is as follows: "What ratios of low molecular weight acids and vegetable acid would replace coconut relative to high viscosity soaps?"

Mr. Aylesworth: The particular fatty acid we used as a standard is a low linoleic oleic acid. The maximum soap content for a free-flowing soap of this acid is approximately 18 per cent. Commercial fatty acids high in linoleic acid will go somewhat higher in viscosity before reaching the breaking point, and thus require a somewhat lower proportion of low molecular weight acids to match the liquid soap viscosity of coconut.

Mr. Terry: The next question is also directed to Mr. Aylesworth. "Has any work been done on use of Ricinoleic Acid in decreasing viscosity of oleic and potash soap?"

Mr. Aylesworth: That is a very good question. We have done a limited amount of work on the effect of ricinoleic acid in liquid soap viscosity and I know of little in the literature on this subject. Generally, ricinoleic acid and oxidizied acids will reduce liquid soap viscosity. As you know, the soaps of ricinoleic acid are rather a special case. They do not suds. They are used in sudsless shampoos and products of that type.

Mr. Terry: The next question is directed to Dr. Wittcoff or Mr. Aylesworth. "What other factors in liquid soap performance are influenced by variations in the fatty acids?"

Dr. Wittcoff: I suspect that I had better yield the floor to Mr. Ayelsworth on this question as he seems to be a specialist in that area. Therefore, I will pass the buck.

Mr. Aylesworth: There are a number of other performance factors that are influenced by variations in fatty acid composition in liquid soaps. That is a very interesting subject. Some information is available in the literature and there are some references given in the printed version of the talk on liquid soaps. Sudsing, foam stability, cold test, color, and odor are important in potash liquid soaps and all of these are influenced by variations in fatty acid composition.

Mr. Terry: The next question is directed to Dr. McCorkle. "Can the fatty amines be satisfactorily alkylated with formaldehyde and formic acid?"

Dr. McCorkle: The answer is "Yes", in good yields. During the war there were some people making tertiary amines by this method. It is not necessarily the cheapest way to make tertiary amines, but it can be done very satisfactorily as to yields and quality.

Mr. Terry: The next question is directed to Dr. Wittcoff. "Would you recommend a reference on color stability determination?"

Dr. Wittcoff: There are a number of references and I have them in my briefcase. I cannot quote them offhand, but if the gentleman who asked the question will see me later, I shall be glad to give him the references.

Mr. Terry: The next question is also directed to Dr. Wittcoff. "What differences, if any, exist between vegetable fatty acids and animal fatty acids of like compositions? Can they be substituted for each other?"

Dr. Wittcoff: There are marked differences but in some instances, especially after appropriate processing, they can be interchanged. Hydrogenated vegetable acids, for example, can frequently replace animal acids in certain applications.