Soaps from Organic Bases*

A Revolutionary Development in the Art of Organic Synthesis

BY R. B. TRUSLER†

THE combination, or chemical union, of a metal or basic group of any kind with a fatty acid produces a salt. If the fatty acid is one consisting of a relatively large number of carbon atoms, such a metallic salt is called a soap. The term "soap" in fact, is rarely applied to salts wherein the fatty acid contains less than nine carbon atoms, and in technology twelve carbon atoms are generally regarded as constituting the practical lower limit for soap-forming fatty acids. The most available soap-producing fatty acid is oleic acid. All grades of oleic acid on the market consist chiefly of true oleic acid together with isomers of apparently the same composition. The two solid fatty acids, stearic and palmitic acids, are next in abundance. Occasional special applications involve soaps made from linoleic acid and from lauric acid, and more rarely from numerous less available fatty acids that cannot be described here. In a general way, because of the indefinite gradation in the physical properties of the salts of the fatty acids, a soap-forming fatty acid may be defined as one whose sodium or potassium salt in water solution produces a foam when shaken. A more exact definition cannot easily be given, for it would involve consideration of the durability of the foam, the temperature, the concentration, and other conditions.

Salts produced by the combination of an organic base with a soap-forming fatty acid belong to the family of soaps just as correctly as do the salts obtained from any alkali or metal and the same fatty acid. An organic base may be described as a collection of non-metallic atoms arranged in a definite, invariable grouping, and which exhibit sufficient basicity to combine with an acid to produce a salt. The organic bases vary greatly in their basicity, i. e., in their combining power. For this reason some organic bases give stable compounds with only mineral acids and certain stronger (more highly ionized) organic acids, and do not combine appreciably with the soap-producing fatty acids. There are numerous organic bases, however, which combine with the heavy fatty acids to produce exceedingly interesting and important types of soaps.

Upon this occasion only the soaps made from organic bases containing one or more nitrogen atoms will be considered. These basic organic compounds are obtained mainly by synthetic chemical means through the substitution of some organic group in place of one or more of the hydrogen atoms normally attached to the nitrogen atom of the ammonia molecule. The replacement of one or more of the hydrogen atoms attached to the nitrogen nucleus makes possible the production of alkylamines and arylamines possessing marked basic properties. An alkylamine always is obtained when one or more of the hydrogen atoms attached to the nitrogen nucleus is replaced by

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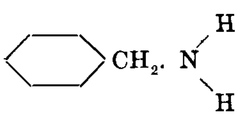
an alkyl, sometimes called aliphatic group. Hence the alkyl group methyl, CH_3-, occurs in

Monomethylamine, $CH_3-N<^{H}_{H}$,

Dimethylamine, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}>N-H$, and

Trimethylamine, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}>N-CH_3$

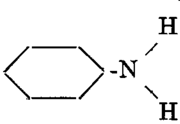
Similarly, the ethyl and propyl groups occur in the ethylamines and propylamines, etc. A single alkyl group may be shared between amine groups. A good example of this is ethylenediamine, $NH_2.\ CH_2.\ CH_2-NH_2$. Also, the alkyl group itself may have some grouping of atoms in place of one or more of its hydrogen atoms, as in the case of benzylamine,



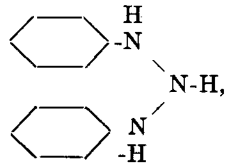
. Then there is the remarkable class of compounds known as the hydroxy-alkylamines, of which triethanolamine,

$N \begin{cases} CH_2\text{-}CH_2\text{-}OH \\ CH_2\text{-}CH_2\text{-}OH \\ CH_2\text{-}CH_2\text{-}OH \end{cases}$, is an example.

The arylamines differ from the alkylamines in that an aryl, or aromatic, or a benzenoid group, replaces one or more of the hydrogen atoms. Aniline,



and diphenyl-guanidine,



are representative compounds in this class of substituted amines.

Ethanolamine Soaps
Theoretical Considerations

The soaps obtained from the ethanolamines promise to become outstanding among the organic base soaps, because of the peculiar properties of the ethanolamine fatty acid compound, as well as the striking and unusual character of these hydroxy-alkylamines themselves.

The ethanolamines, from which ethanolamine soaps are made, are three in number, viz., mono-, di-, and tri-ethanolamines. These compounds are synthesized from ammonia and fundamentally are substituted ammonia compounds, in which one or more of the hydrogen atoms of the compound $N\text{-}H$ (with two further H atoms on N) have been replaced by the ethanol group, $HO\text{-}CH_2CH_2$-. Hence, by the replacement of one hydrogen in ammonia, there results monoethanolamine,

$HO\text{-}CH_2CH_2.\ N<^{H}_{H}$,

which is chemically classified as a hydroxy-alkylamine. Since each of the hydrogen atoms can be replaced by an ethanol group, three ethanolamines are obtainable.

The chemical formulas and boiling points of, these ethanolamines are as follows:[1]

	Formula	*Approximate Molecular Weight*	*Boiling Point*
Mono-ethanolamine	$\begin{matrix}H \\ & \diagdown \\ & & N.CH_2CH_2OH \\ & \diagup \\ H\end{matrix}$	61.07	171°C. at 757 mm.
Di-ethanolamine	$H\text{-}N\begin{matrix}\diagup CH_2CH_2OH \\ \diagdown CH_2CH_2OH\end{matrix}$	105.12	217°C. at 150 mm.
Tri-ethanolamine	$N\begin{matrix}\diagup CH_2CH_2OH \\ -CH_2CH_2OH \\ \diagdown CH_2CH_2OH\end{matrix}$	149.16	277°C. at 150 mm.

The three ethanolamines differ slightly in their physical and chemical properties. They are miscible in all proportions with water, the ordinary alcohols, acetone and its homologues, glycerin, glycol, ethylene chlorhydrin and propylene chlorhydrin, and in general with many oxygenated organic compounds. Among the exceptions to this classification are ethyl ether and some of the aldehydes, in which the ethanolamines are scarcely soluble. Mono-ethanolamine is a colorless liquid, slightly viscous and possesses a faint but agreeable ammoniacal odor. It is one of the most hygroscopic substances known. Di-ethanolamine is also a colorless and odorless liquid. It is viscous like glycerin. Tri-ethanolamine, when pure, is a white, crystalline solid at room temperature. Other physical properties of the ethanolamines, including pH values, will be determined and reported in the future.

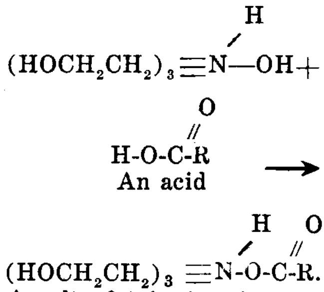
The ethanolamines are basic compounds, shown by their structural formulae. When dissolved in water, they are strongly alkaline to phenolphthalein. Titration with standard hydrochloric acid has shown that one molecular weight of any one of the ethanolamines is equivalent to one molecular weight of sodium hydroxide in combining with an acid. The tri-ethanolamine appears to be more basic than the di-ethanolamine, which, in turn, seems to be more basic than the mono-ethanolamine. The exact relationships will be revealed when the pH values are known.

The combination of any one of the ethanolamines with a fatty acid also results in a neutral compound. A study of the reaction has shown that, during neutralization of these hydroxy-amines, either in solution or in anhydrous conditions, the tertiary nitrogen becomes quaternary in the same fashion as the nitrogen atom in the ammonia molecule when neutralized under similar conditions. For example, in water solution it is evident that tri-enthanolamine is hydrated by adding one molecule of water, as

$$\left(\begin{matrix}HOCH_2CH_2\diagdown \\ HOCH_2CH_2 - \\ HOCH_2CH_2\diagup\end{matrix} N\text{-}H\right) OH$$

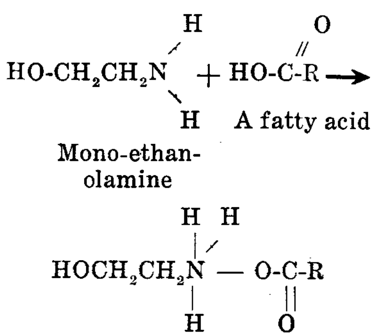
[1] These boiling points were determined by the Carbide and Carbon Chemicals Corporation's Multiple Industrial Fellowship at Mellon Institute.

This combines with an acid in the same manner as ammonium hydroxide, as follows:



A salt of tri-ethanolamine

The reaction between anhydrous ethanolamine and an anhydrous acid yields the same result, since the nitrogen atom again changes valence. It has been found that a molecular equivalent of any one of the ethanolamines combines with exactly one molecular equivalent of an organic acid; and if the organic acid is one of the soap-producing fatty acids, the resulting product is a soap. The reaction may be illustrated by the following equation:



A soap of mono-ethanolamine

The compounds made in this manner were found to be anhydrous. The absence of any water of reaction showed that there was no formation of esters by the acid condensing with the hydroxyl group.

Preparation of Ethanolamine Soaps

In the course of his researches Koganei[2] found that mono-ethanolamine (or beta-amino-ethanol) was sufficiently basic to react with stearic and oleic acids, to produce compounds having decided soap-like properties. This work was done when mono-ethanolamine was prepared by tedious academic means. A few years later, when the ethanolamines were approaching commercial availability through a new chemical synthesis, the preparation of all types of their soaps on a large scale became possible, thus permitting a study of them and their technical applications[3].

There are three possible homologous types of ethanolamine soaps, depending upon which one of the three ethanolamines is used. However, for technical purposes, a mixture of the three can be used advantageously, because they are quite similar in their properties. This mixture, which consists of approximately 75 to 80 per cent tri-ethanolamine, 20 to 25 per cent di-ethanolamine, and 0 to 5 per cent of mono-ethanolamine, has a price advantage over any one of the constituents in that there is no additional cost for fractionation, which, of course, would be necessary if the individual components were required separately. The mixture of these homologues is therefore offered to the trade under the name of "Ethanolamine." While we are interested in the soaps from the individual ethanolamines themselves, we are most interested in the soaps involving the technical ethanolamine, which, incidentally, is obtainable in a high state of

[2] Koganei, Biochem. J., 3, 19 (1923).
[3] The writer was preceded in this study by Dr. O. F. Hedenburg, another Industrial Fellow of Mellon Institute.

purity. Any one of the three ethanolamines as well as technical "Ethanolamine" combines readily with fatty acids to produce soaps. In order to prepare any one of the ethanolamine soaps, it is best to determine the basicity of the ethanolamine by titration in water against a standard acid. This procedure will allow the calculation of the concentration of the particular hydroxy-alkylamine and also takes into account the presence of moisture. The acidity, or combining value, of the fatty acid should also be determined according to a standard method for titrating a fatty acid in alcohol. After these two values have been found, weighed quantities of both ingredients may be combined. It would be convenient, indeed, if approximately correct quantities of both ethanolamine and the fatty acid could be run into the reaction kettle, and then the final necessary amount of either ingredient could be added to bring about a neutral product, as shown by testing portions of it by an indicator. But this method so far has proved to be unreliable, because even with methyl red in alcohol the color change from red to yellow occurs so slowly that uncertain results are had.

The liquid fatty acids, such as oleic acid, permit the easy preparation of ethanolamine soaps. For example, let us consider the preparation of ethanolamine oleate from the technical oleic acid, which may be the "saponified" or the "distilled" variety. Analyses of the oleic acid to be used have shown it to have an acidity of 97.5 per cent in terms of oleic acid, and the ethanolamine has been found to have such alkalinity that 100 grams will combine with 215 grams of pure oleic acid[4]. Then, for every 100 Kilos of ethanolamine there must be added $\frac{215}{97.5}$ or about 220.511 Kilos of oleic acid. The oleic acid is run into the container, which should be provided with a strong and slowly revolving stirrer. The entire amount of ethanolamine can be run in before stirring is begun. When stirring is finally started and the two ingredients are brought into intimate contact, reaction occurs with sufficient heat to keep the contents mobile during stirring. External heat does not promote the combination. Inasmuch as neither of the components appreciably vaporizes, there is no loss during the reaction. Water increases the viscosity of these soaps, and hence the ethanolamine should not contain over 10 per cent moisture, and preferably should be nearly anhydrous, otherwise stirring the reaction mixture will become more difficult. The writer wishes to mention again that the two ingredients unite exothermically, showing a decided chemical reaction.

Combining solid fatty acids, such as stearic acid, with the ethanolamines requires slightly different treatment. In order to mix intimately a solid fatty acid with an ethanolamine to bring about complete reaction, two different procedures are available, namely: (1) The solid fatty acid may be melted and heated to about 60°, and into it is stirred the correct quantity of ethanolamine, which has also been warmed to about 60°. This preheating plus the heat of reaction

[4] While the molecular weight of oleic acid is about 282.27, and the molecular weight of triethanolamine is about 149.16, it has been mentioned that technical ethanolamine contains some of the lighter molecular weight ethanolamines, which increase the ratio of oleic acid to ethanolamine above the molecular proportions of 282.27 to 149.16.

will keep the soap sufficiently soft to allow thorough stirring, otherwise the viscous product will solidify. (2) the stearic acid, or other fatty acid, may be dissolved in a solvent, such as denatured alcohol, to which the ethanolamine is then added with stirring. The soap may be recovered by evaporating the solvent.

Physical Properties of Ethanolamine Soaps

The consistency of any one of the ethanolamine soaps when anhydrous or nearly anhydrous, depends more upon the nature of the fatty acid employed than upon the particular ethanolamine. The oleate of mono-ethanolamine has the consistency of petroleum jelly, while the oleates of di- and tri-ethanolamine are only slightly more viscid. Compared to these, mono-ethanolamine stearate is a hard, wax-like solid.

The soaps prepared from ethanolamines are colored pale yellow to reddish brown, depending upon the purity and color of the fatty acids employed. Generally speaking, all these compounds have an agreeable, soapy odor.

The soaps made from ethanolamines and the higher fatty acids, such as oleic and stearic acids, are soluble in a great variety of organic solvents, which is one of their unusual and outstanding properties. They are dissolved readily by benzene, toluene and similar compounds. Turpentine, alcohols, glycol, glycerine, ketones and many aldehydes are excellent solvents for these soaps. It is surprising to note that even heavy petroleum products, such as lubricating oils and petrolatum, will dissolve considerable amounts of these soaps. In most cases, excepting the heavy oils, the ethanolamine soaps are soluble in the solvents in all proportions, yielding transparent solutions.

Dilute water solutions of the ethanolamine soaps are opalescent to milky, resembling somewhat sodium soaps. The oleate in water froths readily and maintains its soapy character upon standing, but the stearate and, to a less extent, the palmitate slowly revert to the original components, with subsequent partial separation of the fatty acid.

Ethanolamine oleate is capable of taking up a considerable amount of water and remaining jelly-like. The addition of water first causes an increase in the consistency of the soap, this effect continuing until the weight of the water absorbed is about equal to the weight of the soap. Further addition of water renders the soap more plastic and somewhat creamy.

Ethanolamine stearate behaves differently than the oleate upon hydration. Upon the absorption of water, the hard wax-like soap softens, becomes opalescent and reminds one of an agar-agar gel in appearance and consistency.

Applications of Ethanolamine Soaps

The study of the applications of the ethanolamine soaps has chiefly concerned the oleates because of their ease of handling. These oleates are nearly liquid soaps and have comparatively high stability in the presence of water. The two classes of soaps, those from liquid fatty acids and those from solid fatty acids, are not interchangeable in their applications, each one having rather well defined adaptations.

Ethanolamine Oleate as an Emulsifier.—Ethanolamine oleate possesses striking emulsifying ability in promoting oil-in-water emulsions. These emulsions can be made in any one of the known technical ways, but a very simple and efficient method may be employed. The amount of ethanolamine oleate required for the emulsification of an oil depends largely upon the nature of the oil involved. Some oils emulsify with ease as compared to others; for example, linseed oil is much more readily emulsified than olive oil, and therefore requires less soap. This same difference has been observed in the case of mineral oils. In a general way, however, it may be said that from 6 to 8 per cent of soap on the basis of the oil used is sufficient for making a good emulsion. The oil to be emulsified is weighed out in a suitable container. About six to eight parts of ethanolamine oleate per hundred parts of oil are dissolved in the latter during warming and stirring. A transparent or nearly transparent solution of soap in oil results, which may be stored for a stock from which emulsions may be prepared as needed. In order to prepare the emulsion, it is only necessary to add the desired amount of water in the following manner. Supposing an emulsion of 80 per cent of olive oil in water is desired. Water is slowly stirred into the oil containing the dissolved soap. At first the liquid becomes cloudy and somewhat thicker. Further addition of water with stirring will bring about a creamy paste, and when about ten to fifteen parts of water have been added a creamy emulsion results. The balance of the water may be quickly put in. This will produce a heavy, quite permanent emulsion that can be diluted to any desired concentration. In this way a concentrated stock emulsion may be kept on hand from which thinner emulsions can be made when required.

Vegetable oil emulsions of this nature appear to have many applications for non-edible purposes. Excellent emulsions for textile oiling and fiber lubrication have been prepared from olive and palm oils.

Mineral oils may be similarly emulsified. Usually a little more soap is required than for vegetable oils, but the necessary amount can readily be found by experimentation. Mineral oil emulsions of this nature have shown some desirable features for cutting and grinding purposes.

Owing to the solubility of the ethanolamine soaps in petroleum products, some very interesting special applications have been tried on an experimental scale. It has been found that small amounts, in the proximity of 0.3 to 1 per cent of these soaps, dissolved in lubricating oils, increase their viscosity to a great extent. Oils are thus rendered non-running and become suitable for pressure oiling systems (not for internal-combustion engines) and as cup and gear greases.

A convenient and efficient means for removing oil and grease from articles and clothing can be had by dissolving about 10 to 20 per cent of the oleate in a convenient solvent, such as naphtha, carbon tetrachloride, and the like. A solution such as this has been successfully used in cleaning greasy walls, woodwork mechanisms, automobile bodies, and parts covered with grease and oil by brushing or rubbing it over the surfaces to be cleaned. After the solvent has evaporated, the grease and oil can be often completely removed by washing with water, because the grime is removed as an emulsion as the soap is taken up by the water. Ethanolamine oleate in carbon tetrachloride (or ethylene dichloride) will be found useful in removing grease spots from garments. Before the fabric is wetted, the grease spot is moistened with the ethanolamine soap — carbon tetrachloride solution. This will penetrate grease, fresh paint and the like; and after the solvent has evaporated, the application of water with a little rubbing will emulsify the oil content of the stain so that it can be removed.

By far the most important application of ethanolamine oleate seems to be its adaptability for dry-cleaning fabrics and wearing apparel. While this study is still in the experimental stage, sufficient satisfactory observations have been made over a period of several months to warrant the prediction that the soap will be technically valuable. The fact that ethanolamine oleate is readily soluble in naptha over a wide range of concentrations is a feature that makes it especially important, since no special formulas are required in preparing a dry-cleaning soap and it is not necessary to employ an excess of the fatty acid to keep the soap in solution as is the practise for sodium, potassium, and ammonium soap compositions generally used for dry-cleaning purposes. This implies a corresponding decrease in the development of rancid odors in garments after cleaning, since there is no excess fatty acid to be rinsed out. The soap remains in solution in the solvent in the presence of small amounts of moisture which is a desirable feature for drycleaning soaps[5]. For cleaning felt and wool hats where the soap in naphtha is applied particularly good results have been obtained. The naphtha solution of ethanolamine oleate exhibits the striking characteristic of foaming or frothing much like water solutions of sodium soaps, though, of course, to a less extent.

Other Suggested Uses for Ethanolamine Soaps.—Inasmuch as ethanolamine is a surface tension depressant of real merit, it is possible that ethanolamine oleate can be employed as a wetting out agent, or even as a surface tension depressant for special needs.

Experience has shown that ethanolamine has unusual fiber penetrating power, especially in water solution. In order to render this penetrating action available, so that the compound may be used as an introfier, or carrier, in nonhydrous, oily systems, it is suggested that the oil-soluble ethanolamine oleate be used for this purpose.

The excellent emulsifying ability of ethanolamine oleate has been described. It is suggested that this feature be applied for the preparation of concentrated emulsions for veterinary purposes, such as cattle sprays, and poultry, house disinfectants and insecticides. Experience has thus far shown ethanolamine soap to be non-toxic and non-irritating for external use.

Water suspensions of clays and of other finely divided minerals have been found to be stabilized by the addition of small amounts of ethanolamine oleate. Ceramic uses are therefore suggested. A similar application might be made in the case of oil paints. It may be found that a small amount of the anhydrous soap dissolved in the oil would render a more permanent suspension of the pigment, or perhaps aid in preventing the pigments from forming a dense layer in the bottom of the container as they settle out.

The observation of the penetrating and softening action of ethano-

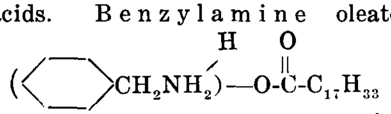
[5] Hatfield & Alliott. J. Soc. Dyers Colorists, 44, 170 (1928).

lamine upon hair led to the preparation of shaving creams with this soap replacing part of the sodium and potassium soaps. The technology of shaving creams involving ethanolamine soap has not been worked out, but the experience to date suggests the use of ethanolamine oleate in creams that are not excessively superfatted.

Other Alkylamine Soaps

Simple alkylamines, such as the methyl and ethylamines and benzylamine, combined with fatty acids to form soaps[6]. Ethyl and methylamine soaps have properties nearly identical with the corresponding ammonium soaps.

Benzylamine readily forms liquid to viscous soaps with the fatty acids. Benzylamine oleate



is a pale yellow soap with a viscosity like glycerin. It has a peculiar but agreeable odor, somewhat resembling nasturtium. This soap is peculiar in that it appears to be as readily soluble in oils and organic solvents as it is in water. It foams in water and allows the preparation of good emulsions. At present the cost of benzyl-, ethyl-, and methyl-amines is far too great to permit their use in the manufacture of commercial soaps.

Ethylene diamine, a double amine whose composition is represented by the formula,

$$\begin{matrix} H & & H \\ & \searrow N\text{-}CH_2\text{-}CH_2\text{-}N \swarrow & \\ H & & H \end{matrix}$$

has both commercial and technical possibilities. The synthesis of the compound has been accomplished by an improved process which will permit commercialization when uses are found for it. As the formula shows, it can combine with one or two fatty acid molecules. One amino group is decidedly basic; but after combining with a fatty acid to give a mono-basic soap of the type $NH_2.CH_2CH_2NH_2(H)\text{-}O\text{-}C(=O)\text{-}R$, the second amino group forms stable compounds only with the stronger fatty acids.

The mono-oleate and monostearate of ethylene-diamine are strongly basic in water solution and froth readily. They are soluble in alcohol, but poorly soluble in petroleum products and in benzene and its homologues. A highly basic, non-metallic soap, such as either the oleate or stearate of ethylene-diamine, is suggestive of desirable technical applications. It should be mentioned that the monostearate of ethylene-diamine is crystalline and flakey, while the two oleates are viscous liquids.

Soaps from Arylamines

Arylamines in general combine with fatty acids to form soaps. This comparatively new field is yielding products of unusual interest and importance. Attention should be called to the soaps of the cinchona alkaloids[7], which are commercially known as "Konate." These cinchona soaps, which are soluble in petroleum distillates and in various other organic solvents, have been found to be most efficacious agents for mothproofing fabrics and furs. The study of many arylamine soaps, their nature and application, is now being undertaken by the writer and the results will be reported later on.

Resumé

Soaps have been made from fatty

[6] Gibbs, J. A. C. S. 28, 1410 (1906).

[7] Jackson and Wassell, Ind. Eng. Chem., 19, 1175 (1927).

acids and organic bases containing nitrogen. The soap-forming bases are alkyl substituted amines and aryl substituted amines. In this paper alkylamines have been especially considered. Among them the hydroxy-alkylamines known as the ethanolamines have outstanding importance.

Ethanolamine soaps have diversified properties which may later bring them into technical importance. Among the prospective uses are the following:

(1) They are excellent emulsifiers for vegetable, animal and mineral oils.

(2) They are thickeners for lubricating oils.

(3) Incorporated in special compositions, they have detergent and cleaning utility.

(4) The oleates are efficient dry-cleaning soaps, due to their solubility in organic solvents and to their specific detergent action.

(5) Their great solubility in almost all liquids will undoubtedly eventuate in other industrial applications.

New Oilseed Crushing Mill in Norway

According to the Norwegian Trade Journal, the Nordiske Fabriker, De-No-Fa A/S have decided to erect an oilseed crushing mill in connection with their works at Fredriksstad, Norway.

This firm is the principal operator in the international whale oil pool. It is considered that, in conjunction with their existing mills at Oslo and Stavanger, the new mill will be able, not only to satisfy the requirements of the Norwegian market in regard to vegetable oil, but will also be able to export such oils. The share capital of the De-No-Fa will be enlarged by the issue of three million kroner. It is stated that this amount has already been guaranteed by the principal shareholders.

Olive Oil Plant Enlarged

Work recently began on a forty by forty-five foot, two story tile storage building to be added to the Rossville (Cal.) olive oil factory in order to care for the 1928 crop. Three years ago when Charles Livoti started the production of olive oil the present factory produced 4,000 gallons of oil. Two years ago the output was doubled, and last year it amounted to 35,000 gallons. With 1928 crop indications excellent the Rossville factory expects to utilize all the additional space being provided.

New Process for Sulphonating Oils, England

A British patent has just been issued to E. C. R. Marks of London on behalf of the Chemische Fabrik Stockhausen et Cie., Grefeld, Germany, wherein oils, fats or fatty acids or mixtures thereof are sulphonated in the known manner and after removal of the dilute acid, the resulting product is mixed with water or dilute acids and allowed to stand until no further separation takes place. A neutral or indifferent solvent such as trichlorethylene may be added before, during, or after the sulphonation, whereby two layers are obtained, one containing the unattacked or slightly attacked component and the other, sulphuric acid esters. The reaction is preferably carried out with increased quantities of concentrated sulphuric acid at a temperature below 150° C. Examples of the process are given in which castor oil is sulphonated.