# Applications of Fatty Acids in Metallic Soaps

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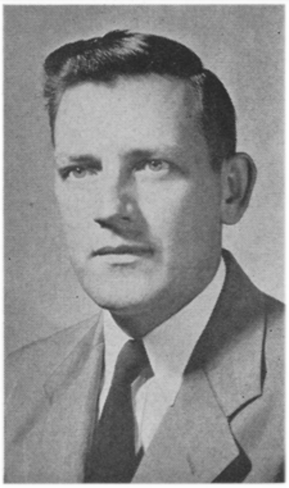
THE applications of fatty acids in metallic soaps are of considerable importance. Producers of fatty acids and manufacturers of metallic soaps are aware a) that the metallic soap field represents a sales outlet for approximately twenty-five to thirty million pounds of fatty acids per year, b) that fatty acids play a very important part in the properties and end uses of metallic soaps, and c) that there must be continuous cooperation between suppliers and users of fatty acids on matters of quality, grades currently available, and any new modifications which may become available. Metallic soaps are defined by Elliott (1) as "the alkali, alkaline-earth, and heavy metal salts of mono-basic complex organic acids." Bossert (6) lists some 25 metals and 12 acids which are commonly used in the production of metallic soaps. This discussion will primarily be concerned with the manufacture, control, and uses of stearates. The effect that fatty acid characteristics have upon each of the above aspects will be stressed. Brief references to oleate, linoleate, and tallate types of soap will be made.



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### Manufacture

Stearates and other metallic soaps can be manufactured by several processes. The simplest process is the so-called fusion method in which metallic oxides, hydroxides, or weakly acidic salts are contacted and interacted directly with fatty acids at elevated temperatures. Mild steel or stainless steel reactors are employed. These are equipped for proper agitation and application of heat. Precautions are taken to obtain controllable and uniform reaction. As water is driven off, the reaction is completed to give the soap product in form of a molten mass. This is then cooled, crushed, pulverized, classified for desired particle size, and packaged. Stearates prepared in this manner are not of purest white color and have the appearance of a fine but dense powder. They are however substantially free of moisture and foreign salts.

In the precipitation method a dilute soluble soap solution is first prepared by reacting caustic soda with the selected fatty acid. A separately prepared salt solution of the desired metal is then added to the soluble soap solution to bring about precipitation of the metallic soap. This method is usually applied on a batchwise basis, but a recent patent (2) describes a continuous mode of operation.

Some of the operating variables affecting the precipitation process are known to be concentration of solutions, temperature, rates of addition of reactants, and efficiency of agitation. The type of filtration equipment used, efficiency of washing, temperature and method of drying, method of grinding, etc., also have a distinct influence upon the results obtained.

Figure 1 illustrates the effect of concentration, particularly how the amount of excess caustic soda governs the type of aluminum stearate obtained.

$$\mathrm{HSt} + 3\,\mathrm{NaOH} \longrightarrow \mathrm{NaSt} + 2\,\mathrm{NaOH} + \mathrm{H_2O}$$

$$\mathrm{NaSt} + 2\,\mathrm{NaOH} + \mathrm{Al^{+++}} \longrightarrow \underline{\mathrm{Al\,(OH)_2\,St}} \rightarrow\ + 3\,\mathrm{Na^+}\ \text{(Al Mono Stearate)}$$

$$2\,\mathrm{HSt} + 3\,\mathrm{NaOH} \longrightarrow 2\,\mathrm{NaSt} + \mathrm{NaOH} + \mathrm{H_2O}$$

$$2\,\mathrm{NaSt} + \mathrm{NaOH} + \mathrm{Al^{+++}} \longrightarrow \underline{\mathrm{Al(OH)St_2}} \downarrow\ + 3\,\mathrm{Na^+}\ \text{(Al Di Stearate)}$$

$$3\,\mathrm{NaSt} + 3\,\mathrm{NaOH} \longrightarrow 3\,\mathrm{NaSt} + \mathrm{H_2O}$$

$$3\,\mathrm{NaSt} + \mathrm{Al^{+++}} \longrightarrow \underline{\mathrm{AlSt_3}} \downarrow + 3\,\mathrm{Na^+}\ \text{(Al Tri Stearate)}$$

FIG. 1.

These types (shown in overly simplified form) are commonly classified as mono, di, and tri, and "in-between" grades are also prepared.

The greatest proportion of the total stearates production is made by the precipitation process. Products so produced are of fine particle size, light and fluffy. Excellent white color is attained because materials of construction throughout a typical plant using this process are wood, galvanized iron, rubber, and stainless steel.

Several factors will affect a decision as to which type of procedure to use for manufacture of any given product. The most important factor is the end-use to which the product is subjected. For "electrical applications" in plastics and rubber the practically zero moisture and salt contents of fused soaps dictate their use. In other applications, for example in the cosmetic industry, the fine particle size, the soft and fluffy nature, and the high spreading rate of precipitated products are demanded. The cost of production by the precipitation method may be slightly higher than that by the fusion method because the former requires somewhat greater capital outlay for equipment and greater amount of labor per pound of product produced.

Certain metallic soaps are marketed in solution form. These products generally come under the categorical designation of "Driers." They are prepared by the above described fusion and precipitation processes with the following modification. After the metallic soaps are formed by fusion or precipitation reactions, they are "solubilized" in mineral spirits, mineral or vegetable oils, and other carriers. The precipitation process can be carried out in a patented two-phase water-naphtha system (3), in which metallic soap as formed becomes soluble in the naphtha layer while the aqueous layer separates and carries away undesirable by-product salts.

## Quality Control Considerations

Control of raw materials, and we particularly emphasize control of fatty acids, is a most important aspect of metallic soap production. The nature of the fatty acid industry is such that the variables of origin (animal, vegetable, and marine), processing treatment (pressed, hydrogenated, etc.), and blending may lead to many, many available grades. In a previous paper (4) we indicated that our company purchases as many as 30 different grades of stearic acids. The physical form as received and handled may be flaked, beaded, slab, or liquid. The general purchase specifications used for each of these are rather simple and are no doubt well known. We specify and routinely control characteristics, such as minimum acid and saponification numbers, titer range, iodine number, and maximum color. Since the specific fatty acids used have a very important effect on properties of the finished soaps, the above tests merely act as the roughest sort of screening devices to catch possible gross errors in shipments. To a considerable extent we rely upon integrity of suppliers to supply uniformity from shipment to shipment because subsequent performance testing of finished products for control of raw materials is necessarily costly and time-consuming. To date the reproducibility of properties from shipment to shipment for specific acids has been excellent.

During the manufacture of soaps by fusion, primary control attention is given to following the decrease in acid number as the metallic oxide or hydroxide is gradually added. In many instances the exact degree to which the fatty acid is neutralized (without introducing excess unreacted alkali) is critical.

The course of the precipitation reaction is controlled a) by careful measurement of the total amount of caustic (necessary stoichiometic amount plus exact amount of excess desired) to carry out the soluble soap step and b) by carefully and exactly reaching the desired final pH of mother liquor as metal salt solution is added to bring about metallic soap formation. In the subsequent "finishing" operation which comprises filtering, washing, drying, and grinding, routine control attention must be given to such factors as amount of retained solubility salts, amount of retained moisture, average particle size, and particle size distribution.

In the production of metallic soap solutions briefly mentioned above, the principal control effect is directed toward attaining desired exact metal content. Other criteria, such as color and viscosity, are also carefully controlled to make products of maximum utility.

Typical properties specified and maintained on finished stearates are total ash content, amount of water-soluble salts, free fatty acid content (determined by acetone extraction and also by alcoholic KOH titration), moisture content, and fineness. Catalogues and technical bulletins of most stearate manufacturers will list these general properties for the various grades manufactured. The reference to general is emphasized because many of the applications of stearates are of a specialty nature and very exacting. Accordingly, a conscientious manufacturer is compelled to do a considerable amount of performance-testing. Various examples can be cited. Grease grade aluminum stearates must be checked for gel strength in mineral oils and for character of the finished grease (this requires a well-equipped grease laboratory and some knowledge of grease-making techniques). Lacquer grade zinc stearates must be checked for dispersibility, flatting and sanding characteristics in lacquer (obviously this requires some knowledge of lacquer formulation and evaluation). Rubber grade zinc stearates are checked for covering power when applied to uncured rubber stocks. Plastic grade stearates are checked for amount of dirt contamination and heat stability. Cosmetic grade stearates are checked for minute concentration of toxic metals, etc.

Marine base stearic acids are generally favored in grease grade aluminum stearates because they contribute good gel strength. Apparently the presence of some $C_{20}$ and $C_{22}$ chain length acids appear to be desirable. Actually a balanced combination of chain lengths from $C_{14}$ to $C_{22}$ appears necessary for proper solubility and gel strength.

The double and triple pressed acids find application in the U.S.P. and cosmetic grades of zinc and magnesium stearates. Hydrogenated tallow types give properties desired in some rubber grade zinc stearates. New and unusual acids with absolute minimum content of trace metals and double bonds appear to be of interest for the high heat stable grades of stearates presently required by the plastics industry.

Metallic soaps which are made and sold in solution form must generally be checked for catalytic activity (drying power) and initial solubility in paint vehicles. Ultimate stability (non-sludging characteristics) in these same vehicles must also be checked. For each of these characteristics the nature of the fatty acid used exerts a profound influence.

## End-Uses

Typical annual production and sales data for the stearates are shown in Table I.

Soaps of the other saturated fatty acids such as palmitates, laurates, and caprylates may become of increasing importance, but at the present time their volume is such that no statistics of production are available.

TABLE I

Stearates—1952 (1,000's of pounds)

| | Production | Sales |
|---|---|---|
| Al | 8,735 | 8,756 |
| Ba | 181 | 202 |
| Cd | 21 | 21 |
| Ca | 3,763 | 3,726 |
| Pb | 1,302 | 1,164 |
| Li | 318 | .... |
| Mg | 589 | 527 |
| Zn | 5,429 | 5,300 |
| All other | 1,267 | 1,649 |
| Total | 21,605 | 21,345 |

End-uses of stearates can be catalogued according to whether the desirable properties are contributed mainly by the fatty acid portion of the soap or whether the metal constituent is of prime importance. Many of the uses for stearates stem from the fact that they offer a means of getting the essential stearic acid properties in a modified form. Some of these properties of stearic acid are lubricity, water repellency, solubility in hydrocarbons and other solvents, and relatively low melting point. When stearic acids are converted to metallic soaps, the lubricity and water repellency characteristics are retained. The degree of solubility is usually reduced, and the melting point is increased.

The change in solubility may be quite pronounced and may, for example, be evidenced in the form of so-called gelling and thickening action. These properties in turn account for end-uses in such practical products as paints and greases. Reduced solubility makes possible other end-uses such as for flatting agents in paints, varnishes, and lacquers, and sanding aids in furniture sealers. Increase in melting point is directly responsible for the fine particle size of the metallic soaps made from stearic acid. A tabulation of the melting points of the normal stearates would show a range covered by iron stearate at 95°C. and lithium stearate at 210°C.

End-uses dependent upon fine particle size (and making use of the intrinsic characteristics of stearic acids) are exemplified by the following. Zinc, calcium, and aluminum stearates give "water-repellency" to cement, paper, face powder, and other materials when uniformly distributed in a dry state. Aluminum, barium, calcium, lead, magnesium, and zinc stearates serve as molding release agents during the forming of rubber, plastics, powdered metals, and other materials. The same stearates serve as lubricants in wire-drawing operations and as anti-caking agents in fire extinguisher (and other) powders; and they reduce tackiness when applied to uncured rubber.

End-uses brought about primarily by the nature of the metal are illustrated by aluminum and lithium stearates for production of lubricating greases. The former give greases with excellent water-repellency, good adhesion to metal, easy pumpability, good transparency and eye appeal, and relatively low dropping point (approximately 200°F.). Greases made with the latter again have excellent water-repellency but are growing in importance primarily because they can serve as multi-purpose products. Their high dropping point range (350-400°F.) is very useful in high temperature industrial applications, and simultaneously their viscosity-temperature coefficient is such that they can be readily applied and utilized at subzero temperatures. Aluminum soaps have more solubility in hydrocarbon solvents than soaps of other metals. Consequently they are used for preparation of solutions and gels to be used for example for waterproofing of masonry and for pigment suspension in paints.

Barium and lead soaps are heat-stabilizers for polyvinyl chloride type resins, and cadmium soaps are light stabilizers in the same application. Lead stearate is used for control of burning rate in ammunition powders. Cobalt and manganese stearates are used as catalysts in the oxidation of waxes and other petroleum fractions. In these applications the usefulness quite apparently is traceable to a chemical action provided by the metallic constituent of the soap. The stearic acid portion serves as a solubilizer and carrier to introduce the metal in a form and a concentration in which it will be most efficient. References (4), (5), (6), and (7) are given for those desiring further details on actual end-uses of metallic stearates.

From the above one can gain some insight into the nature of product development work in the metallic soap field. We are interested in stearic and other fatty acids (and their modifications) which will give soaps of greater gel strength in greases, and we are interested in acids which will give aluminum soaps of higher melting point so that their field of usefulness in greases may be broadened. We are searching for acids which would help us prepare zinc soaps of still finer particle size. It is well known that when metallic stearates are used for flatting and sanding purposes, they detract considerably from the film integrity of varnishes and lacquers. We would be very receptive to acids which might be helpful in solving this problem. More efficient flatting agents are continually being sought. We would welcome acids of exceptional heat stability so that we could prepare products now in demand by the plastics industry.

The above are just a few of the improvements which are sought by all stearates producers in problems of gelation, solubility, flatting effect, sanding effect, heat stability, particle size, and spreading characteristics. The important role played by the fatty acids used is ever before us. A reference (8), for example, illustrates the effect which different chain length acids have on the properties of zinc soaps used in sanding sealers.

The problems are so many and diverse that fatty acid suppliers cannot expect to make recommendations regarding specific grades to be used for specific end uses. Rather they must a) keep us apprised of the grades which they currently offer and b) keep us informed of any new modifications which may become available.

Production volume of soaps of unsaturated acids is not accurately covered in any published information. Production of metallic soaps from oleic acid is usually small except when our armed forces are purchasing Napalm. (Napalm is an aluminum soap prepared from an oleic, naphthenic, and coconut acid mixture.) Aluminum and other metallic oleates are available in pulverized and solid forms, but manufacturers must cope with problems of handling and storage because of characteristics such as low melting point and susceptibility to aerial oxidation.

The unsaturated soaps are therefore generally utilized in semi-solid and solution form. They have better over-all solubility than the stearates and because of this are utilized as driers for paints and varnishes and as fungicides (copper and zinc soaps) for cellulosic materials. Table II gives the 1952 production tabulations for linoleates on a 100% solvent-free basis. It is also obvious that the soaps of petroleum-derived naphthenic acid enjoy a much greater

TABLE II

Production and Sales of Non-Stearate Soaps in 1952

| | Production | Sales |
|---|---|---|
| Linoleates | | |
| Ca | 669 | 514 |
| Co | 195 | 191 |
| Mn | 244 | 221 |
| All other | 810 | 715 |
| Total | 1,918 | 1,641 |
| Naphthenates | | |
| Ca | 1,398 | 1,252 |
| Co | 3,441 | 3,362 |
| Fe | 332 | 432 |
| Pb | 9,772 | 9,252 |
| Mn | 2,526 | 2,167 |
| Zn | 1,224 | 1,084 |
| All other | 656 | 366 |
| Total | 19,349 | 17,915 |
| Tallates | | |
| Co | 1,883 | 1,869 |
| Fe | 120 | 93 |
| Pb | 1,851 | 2,033 |
| Mn | 700 | 804 |
| All other | 320 | 393 |
| Total | 4,874 | 5,192 |

popularity as driers. There has been a flurry of interest toward so-called odorless paint driers, a number of which are based upon vegetable oil fatty acids. At this time it is difficult to estimate the proportion of paint driers which will eventually be of this "odorless" variety.

Metallic soaps of tall oil have established themselves to some extent in the paint drier field *vs.* the naphthenates (see Table II). They will no doubt continue to grow in popularity in this and other applications as refiners of tall oils continue to make up-graded and well-defined fractions available and as the pressure for low material costs is reflected by customer buyer-resistance.

### Summary

In this discussion we have attempted to cover pertinent factors concerning the production and applications of solid fatty acid soaps, with particular emphasis on how the fatty acid characteristics come into play. We have avoided reference to specific formulations because these must be kept in the realm of metallic soap manufacturers' "know how." Those interested in modifiers and their effect on metallic soaps can find reference material in past issues of the Journal of the American Oil Chemists' Society (for example, reference 9) and in the patent literature.

Reference to theoretical considerations of metallic soap structure has also been avoided as in this area the reader can again find reference material in the Journal of the American Oil Chemists' Society (for example, reference 10).

REFERENCES

1. Elliott, S. B., A.C.S. Monograph Series No. 103, "The Alkaline-Earth and Heavy Metal Soaps," Reinhold Publishing Corporation, 1946.
2. Wilson, E., British Patent 693,741 (1953), Chem. Abst., *48*, 392 (1954).
3. Roon, L., Gotham, W., U.S. Patent 2,113,496 (1938).
4. Wagner, E. F., American Paint Journal, *37*, (21), 68-76 (1953).
5. Wendt, R. E., Official Digest of the Federation of Paint and Varnish Production Clubs, *317*, 378-80 (1951).
6. Bossert, R. G., J. Chem. Educ., *27*, 10 (1950).
7. Wendt, R. E., Official Digest of the Federation of Paint and Varnish Production Clubs, *343*, 604-617 (1953).
8. Parker, K., and Wendt, R. E., Official Digest of the Federation of Paint and Varnish Production Clubs, *328*, 311-318 (1952).
9. Smith, G. H., Rogers, L. B., and Mysels, K. J., J. Am. Oil Chemists' Soc., *26*, 135-138 (1949).
10. Mardsen, S. C., and Mysels, K. J., and Smith, G. H., and Ross, S. J., J. Am. Oil Chemists' Soc., *25*, 454-456 (1948).

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# Lubricating Greases

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THERE was a time 20 years or so ago when some people believed that grease production had reached an all-time peak and production thereafter would decrease because of replacement of greases by lubricating oils. History has proved that belief to be wrong. In fact, the production curve for greases in this country has risen to the point where present-day grease manufacture is of the order of 1,200,000,000 lbs. on an annual basis. There is no immediate prospect that grease production will decrease appreciably.

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Generally speaking, greases are recommended for all types of bearings in the following classes of service:

1. where mechanical design (sometimes accompanied by high operating temperatures) would result in excessive oil leakage, high oil consumption, and, in certain industries, contamination or staining of the finished product.
2. where simplicity of design is required, as for example, in in many of the aircraft applications.
3. where mechanical design fails to prevent the entrance of grit, water, or other contaminants into the lubricated areas. Correctly selected greases can provide an effective seal for bearings operating in dusty atmospheres, such as occur in cement mills and coal mines, and thereby prevent excessive wear.
4. where the application of a lubricant is infrequent, on account of the multiplicity or inaccessibility of the bearings. Such conditions are frequently encountered in line shafts, in conveyor systems, and in overhead cranes.
5. where low operating speeds and heavy loads may hinder the ready formation and continued maintenance of adequate lubricating films. These severe conditions are experienced in steel mills, as for example in the lubrication of roll-necks, as well as in various industrial plants where jaw- and roll-crushers are employed.

### Structure of a Lubricating Grease

Basically, what is a lubricating grease? It is essentially a thickened oil in which particles of the thickening agent, usually soaps, are highly dispersed in the oil. Until recent years the highly dispersed particles were not visible microscopically because in size they were too small for resolution by the conventional light microscope. The usual type of conventional lime base grease, when viewed at a magnification of 1,000x, had the appearance as shown in Figure 1. Very little information was gained regarding the basic structure of the grease, using this technique.

With the advent of the electron microscope, procedures (1) were developed for viewing grease structures at magnifications of the order of 20 times greater than was possible with the light microscope. Under the high-resolving power of the electron microscope, dispersed soap particles of greases were readily made visible. An electron microscopic view of the lime base grease shown in Figure 1, examined at a magnification of 20,000x, is given in Figure 2. The dispersed soap particles, in this instance calcium tallow soap, are of the order of one micron in length and 0.1 micron in width. It is to noted that grease properties are not only dependent on the composition of the lubricant but also on the size and configuration of particles of the thickening agent.