TABLE II

Analyses of Known Mixtures Prepared from Compounds Listed in Table I

Sample	Trimethylene Glycol and Propylene Glycol, %[a] Present							
	Water, %		Trimethylene glycol	Propylene glycol	Total	Found	Glycerol, %	
	Present	Found					Present	Found
C. P. glycerine								
1	5.0	4.9	0.6	....	0.6	0.6	94.4	94.5
2	4.9	4.8	1.1	....	1.1	1.1	94.0	94.1
3	4.9	4.8	2.8	....	2.8	2.8	92.3	92.4
4	4.9	4.8	....	0.9	0.9	1.1	94.2	94.1
5	4.9	4.8	0.9	0.9	1.8	2.0	93.3	93.2
6	4.9	4.7	....	2.5	2.5	2.8	92.6	92.5
7	4.8	4.8	2.6	2.5	5.1	5.3	90.1	89.9
8	4.8	4.8	4.9	....	4.9	4.7	90.3	90.5
High gravity glycerine (containing trimethylene glycol)								
9	0.5	0.5	1.5	0.3	1.8	1.9	97.7	97.6
10	0.5	0.5	2.0	....	2.0	2.0	97.5	97.5
11	0.5	0.5	3.6	....	3.6	3.7	95.9	95.8
12	0.5	0.5	1.1	0.9	2.0	2.1	97.5	97.4
13	0.5	0.5	2.0	0.9	2.9	2.9	96.6	96.6
14	0.5	0.5	1.1	2.5	3.6	3.7	95.9	95.8

[a] The amount of trimethylene glycol present is normally several times the amount of propylene glycol.

Analyses of sweet water concentrates (6) have shown that propylene glycol is present along with trimethylene glycol, and it is difficult to prepare trimethylene glycol free from propylene glycol by distillation from sweet water concentrates. Thus whenever trimethylene glycol is present in C. P. or high gravity glycerines, some propylene glycol may also be present. In the above formula the two glycols are calculated as trimethylene glycol since it is generally present in quantities several times larger than the propylene glycol.

The accuracy of the proposed method was investigated by analyzing known mixtures of glycerol, trimethylene glycol, propylene glycol, and water. The properties and compositions of the compounds used in preparing the known mixtures are given in Table I.

The results of the tests on the known mixtures are given in Table II.

Trimethylene glycol and similar constituents calculated as trimethylene glycol were determined within 0.2% of the amount present. This is greater precision than can be expected from tests between different laboratories. The between laboratories variation expressed as the standard deviation is ± 0.13 for the specific gravity method and ± 0.20 for the Fischer volumetric method (9). Under these conditions single tests can be relied upon with 95% confidence only when the value for trimethylene glycol is more than 0.5%. The certainty of smaller amounts might be established by using the average of 2, 3, 4, or more analyses.

Summary

A method has been developed for the determination of small amounts of trimethylene glycol together with similar constituents in C. P. and high gravity glycerines. The various constituents in known mixtures were determined within 0.2% of the amount present. The method is simple and accurate and utilizes proven A.O.C.S. Methods.

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[Received October 29, 1953]

The Function of Fatty Acids in Metallic Soaps[1]

FRANCIS J. LICATA, Metasap Chemical Company, Harrison, N. J.

METALLIC soaps are compounds of metals and fatty acids, which are characterized by water repellency, solubility in some organic liquids, extremely small particle size, and purity of the metal content.

Although the cation or metal part of these compounds plays an important role in such uses as driers, ceramic glazes, and mildewproofing, the fatty acid fraction has a more important function because it governs the physical properties, such as melting point, particle size, fluffiness, unctuousness, and solubility.

In view of the fact that most of the industrial uses of metallic soaps depend on their physical characteristics, it is apparent that the choice of the fatty acid is an important one. The method of manufacture and the application of metallic soaps to the production of waterproofing compounds, lubricants, paints, varnishes, lacquers, inks, rubber, plastics, and waxes to a large extent depends on the fatty acid employed.

As a rule low titer, liquid fatty acids produce metallic soaps which have low melting points and good solubility while the higher titer fatty acids produce soaps which have rather high melting points, poorer solubility, and greater water repellency.

The methods of manufacture of metallic soaps are definitely related to the melting point of the fatty acid and the metallic soap resulting from it. With liquid fatty acids it is easier to react them with oxides, carbonates, or acetates. The metallic soaps from these fatty acids also have relatively low melting points which allow them to be melted and dried

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[1] Presented at the annual Fall Meeting, American Oil Chemists' Society, Nov. 2-4, 1953, Chicago, Ill.

TABLE I

Various Calcium Soaps

Type	Fatty Acid Iodine Value	Titer °C.	Method of Preparation	Calcium Soap		Solubility in Hydrocarbons
				Physical Form	Melting Point °C.	
Oleic	90	8	Fusion	Lump	R*	Good
Linoleic	190	15	Fusion	Lump	R	Good
Naphthenic	nil	Liquid	Fusion	Lump	R	Excellent
Tall oil	170	15	Fusion	Lump	R	Good
Rosin	200	65	Fusion	Lump	R	Fair
Rosin	200	65	Precipitation	Powder	Variable	Poor
Lauric	2	40	Precipitation	Powder	130	Fair
Stearic	8	55	Precipitation	Powder	150	Poor

* R signifies that this metallic soap is ordinarily fused at room temperature.

easily in the same reaction kettle. The greater solubility of these soaps produces low viscosity solutions hence the solvent may be introduced before drying, and the water which is a product of the reaction may be removed by decantation.

The higher titer, solid fatty acids produce soaps which have high melting points and poor solubility. These are best prepared by precipitation from the sodium soap as fine powders (5). Table I illustrates this by showing the melting point, titer of various fatty acids, and the melting point, solubility, and method of manufacture of the corresponding calcium soap.

The manufacture of metallic soaps on a large scale has been limited by economic factors to commercially available fatty acids or closely related glycerides. As a consequence of this, pure fatty acids have been employed but rarely in this industry although as fractionated fatty acids have become available, the industry has been quick to take advantage of any desirable feature they possess.

The present brief attempt at grouping metallic soaps in accordance with the fatty acid used is made in order to show that when these products are regarded from this point of view, the formulation, method of manufacture, and final application of metallic soaps will appear more rational.

Oleates. At one time the oleates had the lowest melting point and best solubility of the then available metallic soaps. It was possible to manufacture them by the fusion method by reacting the fatty acid with an oxide. It was easily possible for a small operator to make a large number of products in small quantities. Often the consumer made his own metallic soaps *in situ.* The manufacture of lime greases is an instance. In this case the oleic content of the grease contributed smoothness and softness to the grease.

Copper oleate for anti-fouling of ship bottoms, fish nets, canvas, and rope is another. Magnesium oleate was dissolved in dry cleaning solvents because it was believed that it conducts electricity and thus acts as an anti-static agent.

Lead oleate was also used to prepare heavy duty lubricants of the 19th century (3) as well as lead plasters.

Aluminum oleate was more difficult to make; however large quantities were produced to thicken lubricating oils used as castor oil substitutes and as anti-chatter oil for the noisy early Fords. Aluminum oleate as an ingredient of Napalm contributes elasticity as well as thickening properties to gasoline (13). A peace-time modification of this product serves to thicken kerosene for oil well fracturing.

Linoleates—The manufacture of paints and varnishes requires the use of such metals as lead, cobalt, and manganese in a soluble form to act as "driers" for linseed oil. The linoleates are very similar to the oleates with the added feature that their higher degree of unsaturation causes them to be an integral part of the dried oil film. Low melting linseed oil fatty acids produced corresponding low melting point linoleates, which were manufactured by the fusion method. If they became too hard as a result of overheating or polymerization, an additional quantity of fatty acids was used so that the soap could be handled more easily.

A calcium linoleate pulp containing about 70% water is used to this day for suspending paint pigments when incorporated with grinding vehicles (11).

Resinates. Rosin is a solid at room temperature, and the metallic soaps of it or the resinates have a correspondingly higher melting point. Because of this it is possible to manufacture resinates as powders by precipitation as well as lumps by the fusion method. A higher metal content is possible by use of the precipitation method. The powdered resinates have a greater surface and are subject to oxidation which reduces their solubility unless used soon after they are prepared.

The resinates of cobalt, lead, manganese, and iron were used as driers. In the powder form these and other colored resinates, such as, nickel, copper, and chromium are used in the preparation of colored ceramic glazes (4).

The resinates are hard solids that dissolve in linseed oil and mineral thinner, thus they form a base for cheap varnishes. The color of these resinate solutions made them applicable as quick drying colored varnishes for metal objects (10).

Calcium resinate dissolves in rosin to produce a film tougher than rosin alone (2).

Large quantities of aluminum resinate are used for paper sizing (1).

Solates and Tungates. The soaps of soya bean and tung oil have been substituted for resinate and linoleate driers especially in printing ink formulations. However they do not seem to have wide usage.

Naphthenates. The usefulness of metals as driers depends upon their solubility in oils and thinners. Although the metallic linoleates and resinates are much more soluble than the inorganic compounds formerly used to dry linseed oil, they actually were never completely soluble. Through oxidation they would become insoluble, and on aging they would tend to separate out as sludge and thus become inoperative.

The search for completely soluble driers with high metallic content reached a high degree of accomplishment when in 1925 Soligens and in 1932 the Nuodex solutions became commercially available.

Naphthenic acids are saturated cyclic liquid compounds having a characteristic odor. Their metallic soaps have a correspondingly low melting point and good solubility. Because of the saturated nature of the naphthenic acids, they are very stable. The naphthenates are easily manufactured by the fusion method in the presence of mineral thinner. By use of naphthenic acids it becomes possible to manufacture driers which have a definite metal content, permanent efficiency, and compatibility with synthetic resins.

Lead, cobalt, and manganese naphthenates easily displaced the linoleates, resinates, and other driers because as solutions they could be introduced into formulations by simple mixing. No heat with resulting discoloration was necessary (7).

Calcium and zinc naphthenates are used as auxiliary driers, the first to replace lead in some drier combinations and the other to harden films, and as a wetting agent. Iron naphthenate is useful in dark-colored, glossy baked finishes.

Lead naphthenate is used in compounding heavy pressure lubricants.

Cerium naphthenate is suggested when a minimum of discoloration is desired.

Naphthenic acids used in the manufacture of Napalm contribute the factors of stability, low temperature, gelation, and elasticity.

Copper naphthenate forms stable, low viscosity solutions with mineral spirits, which are used for rot-proofing canvas, lumber, rope, and other fabrics.

Tallates. During World War II the limited supply of naphthenic acids was diverted to the manufacture of Napalm. Therefore drier manufacturers were obliged to look elsewhere for raw materials. It was fortunate that the production of tall oil had reached such a relatively high degree of refinement. Metallic tallates were surprisingly good. Tall oil yields soaps which are fused at room temperature and are easily soluble.

In general, the solutions of tallates are more stable than the linoleates or resinates but not as good as the naphthenates. They tend to oxidize and lose solubility. Except in cases of economy the naphthenates when available regained any lost ground.

Octoates. Because 2-ethyl hexoic acid is a synthetic product with definite chemical constants, it is a highly desirable raw material for the manufacture of metallic soaps with dependable properties. It is chemically saturated and is an odorless, colorless, low viscosity liquid. Hence the octoates are odorless, have excellent solubility, and tend to produce colorless or bright-colored, low viscosity and stable solutions.

Octoate driers are excellent; however their higher price limits their application to such formulations calling for absence of odor, minimum color, and unusual compatibility with synthetic resins.

The unusual solubility of the octoates is illustrated by aluminum octoate which gels at room temperature with such good solvents as carbon tetrachloride, turpentine, and toluol. Further evidence is the fact that aluminum octoate will form permanently transparent and elastic gels with kerosene at about 55°C. (131°F.). Five percent of aluminum octoate in kerosene will have a viscosity of about 1,000,000 centipoises at 32.5°C. (90°F.). This high viscosity is maintained indefinitely, and the gel resists thinning by such agents as water. For this reason these gels are used as various types of plugs in oil well treatment.

Aluminum octoate is also employed in paint, varnish, and ink formulations, which require permanent and viscous type of flow (17).

One of the strange features of aluminum octoate is that it will not make grease with petroleum oils even when treated to 150°C. (302°F.).

Stearates. It will surprise a few to learn that stearates may contain only a small fraction of stearic acid. The industry has had to use commercially available types of stearic acid which may contain as much as 55% palmitic and 8% oleic acid. Nevertheless the stearates constitute a most interesting group of metallic soaps whose usefulness depends on the fact that they are almost inert and, in the case of aluminum stearate, because it forms gels and thickens many solvents, oils, resins, and waxes.

Commercial stearic acid is essentially a chemically saturated, white solid having a titer of 50 to 55°C. These properties indicate that the stearates will tend to be high melting point solids with good stability but poor solubility. It is possible to manufacture stearates with a particle size of one micron. This degree of fineness contributes a certain degree of surface activity, water repellence, and lubricity (8).

The several long, non-polar saturated chains of stearic acid attached to the metallic ion are sufficient to inhibit the activity of the cation. Hence stearates are chemically unreactive except that they may be decomposed by acids or alkalies. This inactivity also prevents their solubility unless sufficient energy is supplied by means of heat to liquefy them. Thus they may appear to dissolve in liquids which can withstand a temperature of about 150°C. However on cooling they will come out of solution again as fused lumps or as rigid pastes with the liquid phase.

In spite of their inertness, stearates find many applications which utilize their physical properties. The water repellence makes stearates essential for waterproofing compounds for textiles, rope, and masonry surfaces. Calcium stearate is used to prevent caking of such fine hygroscopic powders as cement, dynamite, sodium bicarbonate, salt, and animal feeds.

The lubricity and small particle size of metal stearates makes them ideal as dry lubricants for wire drawing, plastics compounding and molding, metal powder metallurgy, oil-less bearings, and pharmaceutical tablets.

The flatting of lacquers and varnishes with stearates depends on the fact that these soaps function as inert and discrete particles which rise to the surface to reflect light in all directions and thus produce a dulling effect.

Calcium, magnesium, zinc, and lithium stearates are used in cosmetics for face powders, talcum powders, shampoos, and creams because of their physical properties.

Table II contains the general properties of several stearates and shows how much they differ from other metallic soaps.

Aluminum stearate is by far the most important and has received the greatest amount of attention. This product has the unique property among stearates of dissolving in various solvents to form various types of transparent and stable gels.

With powerful solvents like carbon tetrachloride, turpentine, and toluol, aluminum stearate forms stable transparent and viscous gels at 45°C., which may be used as transparent surface waterprofing compounds. On the other hand, saturated straight chain solvents like mineral spirits require the higher temperature of about 85°C. to dissolve the stearate. However the lack of solvency of this liquid for aluminum stearate is indicated by the syneresis and cloudiness which develops after several days. There is a transition between a finely dispersed solid forming a transparent and elastic gel to a coarser dispersion having an opaque and rigid structure with syneresis. The use of aluminum stearate in paints to prevent settling and hard caking makes use of this phenomenon.

When aluminum stearate is heated with petroleum oil at 125-150°C., it dissolves to form a viscous gel which on cooling to room temperature, undisturbed, sets to a rigid and transparent structure. The resulting soft, smooth, and transparent mass is permanent enough to be useful as a lubricating grease (9). The aluminum stearate in this type of a grease is so finely dispersed that when examined with an electron microscope the stearate particles appear as a cloud without a definite pattern.

Aluminum stearate, like other stearates, can be modified by use of a small percentage of other fatty acids. It has been found that the bodying or grease making power of aluminum stearate is increased to an appreciable extent by the addition of 3 to 10% of caprylic, behenic, dimerized linoleic acid, and others.

Even with resins and paraffin wax 5 to 10% of aluminum stearate will combine to form tougher and less crystalline compounds with a wider melting point range.

Recently aluminum stearate has been suggested for the preparation of jelly brilliantines (12) and for the changing of fluid plastisols to semi-solid plastigels (15).

Lithium stearate is the base for multipurpose greases which are useful over the wide temperature range of —65°F. (—55°C.) to 350°F. (177°C.).

Ricinoleates. Ricinoleic acid from castor oil has an hydroxyl group attached to it which makes this fatty acid different from all other straight chain fatty acids. The presence of the hydroxyl group prevents the solubility of ricinoleates in oils and hydrocarbons although it will dissolve to form viscous gels in castor oil and higher alcohols (14).

Aluminium ricinoleate is an ideal waterproofing agent for textiles because it forms stable, continuous, flexible, and transparent films which resist dry cleaning solvents.

Recently an attempt to popularize the ricinoleates has brought out the fact that some of them may be useful as stabilizers for polyvinyl resins against light and heat discolorations.

Hydroxystearates. The hydrogenation of castor oil is the source of commercial hydroxystearic acid. These metallic soaps are very similar to the stearates in that they may be produced as fine powders with a high melting point, are water repellent, and unctuous. Like the ricinoleates, the presence of the hydroxyl group inhibits their solubility in oils and hydrocarbons.

Lithium hydroxystearate finds application as a low-temperatue grease base because it can be compounded with dibasic esters to produce lubricating greases which can function at a temperature as low as —100° F. (—73°C.).

TABLE II

General Properties of Stearates

Property	Aluminum	Calcium	Lead	Magnesium	Zinc
Specific gravity...	1.010	1.041	1.323	1.028	1.056
Refractive Index	1.36-1.39	1.40-1.50	1.50-1.55	1.50-1.55	1.50-1.55
Softening point..	145°C.	150°C.	100°C.	150°C.	118°C.
% Oxide............	8.0	10.0	28.0 (Pb)	8.0	15.5
% Free stearic acid.....	12.0	nil	nil	nil	nil
Solubility...........	G	PS	PS	PS	I
% Retained on 100 mesh........	0.0	0.0	0.0	0.0	0.0
% Retained on 200 mesh........	2.0	0.0	0.0	0.0	0.0
% Retained on 325 mesh........	5.0	0.1	0.1	0.0	0.0
% Retained on 400 mesh........	....	0.2	....	0.0	0.1

(I) Insoluble. (PS) Partly soluble and may form pastes in hydrocarbons, chlorinated solvents, turpentine, and so forth. (G) Will form gels in hydrocarbons, chlorinated solvents, turpentine, oils, waxes, and resins.

Laurates. Lauric acid is the chief component of coconut oil fatty acids. It would follow that metallic soaps made from coconut oil might be called laurates. For unknown reasons the soaps of coconut oil were called palmitates. However when the lower molecular weight fatty acids of coconut oil are distilled, the residue contains about 90% lauric acid. This is the raw material for metallic laurates. Lauric acid is a saturated compound with a titer of about 40°C. Its metal derivatives therefore are solids at room temperature and have a tendency to be a little more soluble than the stearates and may be prepared either by the fusion method as brittle solids or as powder by the precipitation methods.

Napalm which is an aluminum soap of a mixture of fatty acids contains a large fraction of coconut oil fatty acids, which tend to contribute ease of gelling and greater body or resiliency to the thickened gasoline (6).

The largest use for laurates is in stabilizing vinyl resins. Whenever polyvinyl chloride resins are exposed to light and heat, hydrochloric acid is given off. This is followed by the formation of a conjugated polyene structure which acts as a catalyst to release more hydrogen chloride. In doing so, the resin becomes progressively darker and more brittle.

In view of the fact that vinyl resin plastics are compounded at about 350°F. (176°C.) and because transparent films of these plastics are not expected to change color on exposure to light, it is evident that the use of a stabilizer is a prime necessity.

Many substances have been used to accomplish this. It has been found that 2-3% co-precipitated barium and cadmium laurates in the proper ratio will not only inhibit the release of hydrogen chloride at 350°F. (176°C.) for at least 90 minutes but will also prevent the deterioration caused by exposure to light and at the same time produce a clear film. The use of a chelating agent will help produce greater beneficial synergistic effect (16).

Conclusion

The above consideration of metallic soaps has been conducted from the point of view of the fatty acid used. It is evident that the fatty acid does play an important function in determining the method of preparation, the physical properties, and ultimately the use of metallic soaps.

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[Received October 29, 1953]

Inter- and Intramolecular Polymerization in Heat-Bodied Linseed Oil[1]

R. F. PASCHKE and D. H. WHEELER, General Mills Research Laboratories, Minneapolis, Minnesota

THERMAL polymerization of drying oils occurs by the formation of direct carbon-to-carbon bonds between the polyunsaturated acid groups present in the triglyceride oil molecules. With conjugated polyene acids the dimerization of the polyunsaturated acid groups is undoubtedly by a Diels-Alder addition reaction while with non-conjugated polyenes it has been proposed that thermal conjugation precedes the Diels-Alder addition of conjugated diene to non-conjugated diene. Whatever the mechanism of polymerization of the polyene acid groups, it is well known that dimerization is the principal reaction, with some trimerization, but probably no higher degree of polymerization.

Triglycerides or other polyesters containing two or more polyene acid groups per molecule can therefore polymerize to very high molecular weights, up to infinity (gelation), theoretically. The composition of drying oils capable of extensive heat bodying are qualitatively in accord with this concept of a functionality of approximately one for heat polymerization of polyunsaturated fatty acid groups.

There have been some considerations whether the dimerization (and trimerization) of the polyene acid groups in bodied oils occurs exclusively between acid groups in different molecules (intermolecular dimerization) or whether there is reaction between acid groups in the same molecule (intramolecular dimerization) (1, 2, 3, 4, 5, 6).

Intermolecular dimerization increases the molecular weight by joining two different molecules. Intramolecular dimerization does not increase molecular weight since reaction is between parts of the same molecule. Intramolecular reaction may occur between acid groups in the same unpolymerized triglyceride molecule, or it may occur between acid groups of the polymeric triglyceride, either between acid groups in the same or different triglycerides in the polymeric triglyceride. Either type of intramolecular reaction would result in less increase in molecular weight of the oil than would be expected from the same extent of intermolecular reaction.

Bradley (1), as well as Adams and Powers (2), suggested intradimerization to explain the observed molecular weights which were lower than would be expected from the extent of reaction, as judged by the change in iodine number. In view of the fact that monomeric acid groups with decreased unsaturation are formed from both linoleate and linolenate groups (7, 8, 9), this method is subject to error. This error is in the direction which would account for the observed molecular weights being lower than calculated from the decrease in iodine number.

Barker, Crawford, and Hilditch (10) considered that in the earliest stages the reaction is largely intramolecular. The sudden rise in viscosity in the later stages of reaction, with very little apparent change in linoleate and linolenate content, suggested that there was rearrangement from intra- to interdimerization by ester interchange. They demonstrated that ester interchange did occur slowly at bodying temperatures with non-polymeric triglycerides. They also converted some of the bodied oils to methyl esters and determined the molecular weight of the methyl esters. The theoretical molecular weight of the glycerides was calculated from that of the derived methyl esters. The most viscous oil which they studied was a 5.4 poise linseed oil with an observed molecular weight of 1,276 compared to the calculated value of 1,481. This difference of 14% may indicate some intradimerization, but not very extensive.

Joubert and Sutton (11) separated a light viscosity (1.2 poises) bodied pilchard oil into monomeric triglycerides (65%) and polymeric triglycerides (35%) by molecular distillation. The monomeric triglycerides were converted to methyl esters and distilled to afford only 1.5% of dimeric ester. They also segregated the polymeric glyceride into fractions ranging from 2,000 molecular weight up to 8,800. The fraction of 2,200 molecular weight was converted to methyl esters and found to contain about 67% monomeric and 33% dimeric esters by weight, which would correspond to a dimeric triglyceride (mol. wt. approximately 1,770) compared to 2,200 mol. wt. found.

Thus in this oil the monomeric triglycerides showed only very slight intrapolymerization, and the lowest molecular weight polymeric triglyceride showed no evidence of appreciable intrapolymerization.

Boelhouwer, Jol, and Waterman (12) bodied linseed oil to 33, 73, and 210 poises. The 33-poise oil showed 46% monomeric triglyceride, whose derived methyl esters showed 15% residual dimer plus trimer. The 73-poise oil showed 38% monomeric triglycerides with 29% of residual dimer plus trimer in their de-

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[1] Paper No. 158, journal series, General Mills Research Laboratories, Minneapolis, Minn.