The METALLIC SOAPS

A THESIS

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FOREWORD

To Dr. Hilton Ira Jones, to whose untiring interest and unfailing co-operation the writer owes much, and under whose direction and supervision this work has been brought to its completion, the following pages are respectfully dedicated.

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THE METALLIC SOAPS

INTRODUCTION

The word "soap," at once suggests to the non-chemist the commercial products which for centuries, have been used principally as a cleansing agent. Such detergent soaps are made from some fat or oil such as cotton-seed oil, stearin, olein, palmitin saponified with either sodium or potassium hydroxide. The term soap in the wide sense, however, includes the metallic salts from any of the fatty acids. A few of these metallic soaps have been made and found to have important commercial uses. Ferric soap was first made and used as an ingredient of axle grease. Calcium and magnesium soaps have been used in cup-greases and in preparing materials for candle making. Although a few metallic soaps have been prepared as yet no one systematically experimented even with the metallic soaps of the most common and easily obtained elements and studied their relative properties.

The purpose of this research was to prepare and study systematically the following metallic soaps: manganese, copper, zinc lead, nickel, calcium, cadmium, antimony, strontium, cobalt, barium iron (ferrous and ferric) silver, mercury, arsenic, chromium, bismuth, magnesium, ammonium and lithium determining their properties and if possible finding new uses for the ones which seemed most promising. Dr. H. I. Jones and Robert Du Bois prepared recently an aluminum soap the solution of which they discovered could be used as a wonderful preservative for eggs. It has seemed possible therefore that similar soap solutions might be used as a water-proofing material for cloth, leather, and even metals; that they might prove valuable not only for preserving eggs but for fruits and vegetables as well; that their unusual properties of adhesiveness and insolubility might make them valuable for water-proofing cement blocks and even for rendering cisterns and cellars water tight. It has been the possibility of these and many other similar utititarian uses which has furnished the motive for this work.

HISTORICAL & GENERAL

Soap was not known to the ancient Hebrews and Phoenicians or to the Greeks of the time of Homer, for they washed their garments with the ashes of plants, which was rubbed into the cloth and stamped in with the feet. The people of some nations used the juices of certain plants, until it was discovered that when ashes were heated with lime a substance called "natron" was made, which cleansed the garment much better than the ashes alone. The manufacture of this "natron" and its uses are described by Pliny, the Elder. Although the Hebrews and the Greeks did not seem to use soap or mention it under that name at least, yet in the Bible we find it mentioned. The writers of the Bible, who were not exact historians, however, several times mention soap and quote the supposed phrases of the prophet Jeremiah (who would have lived several centuries before the Christian era), "Though thou wash thee with nitre (natron) and take thee much soap, yet thine iniquity is marked before me." [1] Also, "Who shall stand when he appeareth? For he is like a refiner's fire and like fuller's soap." [2]

Seneca and Pliny in their writings mention two kinds of soap, soft and hard, as used by the Germans. It was then only a Gallic invention used to make the hair bright and glossy, and as a medicine now known as lead plaster. The Germans prepared it from the tallow tallow of goats and the ashes of plants. It is not until the second century of the Chistian era, that we have Galen proposing the use of soap for washing.

The art of soap-making is very old, for in the evacuations of Pompeii a complete soap factory with utensils and saponified material, was found. As early as the ninth century Marseilles did a large trade in soap, but in the eleventh century it had a serious rival in Savona. In the fifteenth century the industry flourished at Venice, and in the seventeenth at Genoa, which together with Savona, Marseilles and Alicante monopolyzed the manufacture of soap. It was not until after 1650 that the soap industry began to develop in England. In Germany the processes were very crude and the industry made no advancement until revolutionized about the ninteenth century by Chevreul's classical investigations on fats and oils, and by Leblanc's process for the manufacture of caustic soda from common salt. It was Chevreul who raised soap-

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[1] Jeremiah 11-22
[2] Malachi 111-2

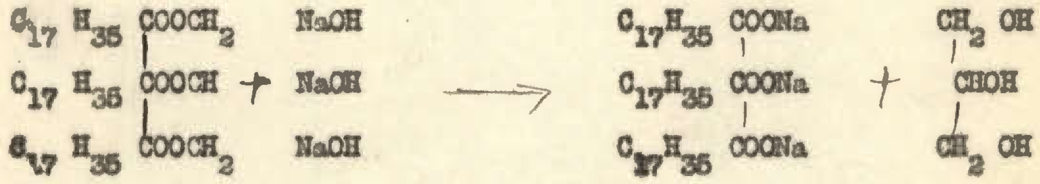
making from the-rule-of thumb methods to a true scientific industry.

With the rise of the soda industry and the increase of the trade in palm oil and coco-nut oil, the conditions in Germany and to some extent in other countries favoured the development of soap-making. At the present time Marseilles, although partly surpassed by the large English factories, still preserves its early fame, which however, the Italian factories have lost. But several times in the past the renown of Marseilles has been dimmed owing to the custom even in the early days of adulterating soap and of loading certain qualities of white soap with enormous quanties of water. This is the reason that for many years, the public preferred the mottled soap, because if could not be so adulterated. This also explains the reason for formulating the laws in France against dishonest soap makers, who in 1790 provoked a general protest of all the population and a petition to the deputies of the States General from all the laundresses of Marseilles to protest, "Against the adulteration of white soap and against the malefactors who adulterate it to increase its weight." It does not appear that things have changed very much during the last 120 years, for, since the introduction of palm oil and coco-nut oil in 1850 the consumer has always paid for a considerable amount of water in place of soap.

Previous to Chevreul's researches on fats (1811-23) it was believed that soap consisted of a binary compound of fat and alkali. Claude J. Geoffrey in 1711 pointed out the fact that the fat or oil recovered from a soap solution by neutralising with an acid differed from the original fatty substance in that it was soluble in alcohol, which was not the case in ordinary fats and oils. The significance of this discovery was overlooked. Equally unheeded was a not less important discovery by Scheele in 1783. He prepared lead plaster by boiling olive oil with oxide of lead and a little water--a process similiar to the soap-boiler process--and obtained a sweet substance which he called "celsuss" but is now known as glycerine. These discoveries of Goeffrey and Scheele formed the basis of Chevreul's researches by which he established the constitution of oils and discovered the true nature of soap.

Theoretically soaps include all metallic salts of the higher fatty acids, but practically the name is given only to the salts of oleic, stearic, and palmitic acids and in general, of the fatty acids contained in natural oils and fats. The important soaps are the potassium and sodium soaps. It was at one time thought that soaps were composed principally of margaric acid, but it has now been shown that this acid does not occur in natural fats. The reason for the confusion was that a mixture of palmitic and stearic acids has the same melting point as margaric acid.

When tallow, lard, palm oil, corn oil, cotton-seed oil or other fatty material is treated with a solution of potassium or sodium hydroxid, a chemical change takes place resulting in the formation of a product soluble in water and possessing properties entirely different from the original fat or oil used. When the soluble product is treated with an acid an insoluble product is formed. If a quantitative test is run it will be found that the substance obtained from the acid treat- is only about 90 per cent of the original weight of the fat. Something therefore has been eliminated during the operation. This loss may be recovered from the acid liquor by evaporation, it has sweet, taste, an oily consistency, and is known as glycerine. The portion which when combined with an alkali is soluble, proves to be made up of compounds such as stearic, palmitic and oleic acids. Thus Chevreul concluded that fats are glycerides of fatty acids. Thus when we make soap we decompose the fatty acid glycerides with caustic alkali and form salts of the fatty acids known as soaps and separate the glycerine. In boiled soap the glycerine is separated, but in half boiled or cold-made soaps it remains as part of the soap. The reaction taking place between the alkali and the fatty glycerides is shown in the following equation:



$$\begin{array}{lcl} C_{17}H_{35}COOCH_2 & & NaOH \\ C_{17}H_{35}COOCH & + & NaOH \\ C_{17}H_{35}COOCH_2 & & NaOH \end{array} \longrightarrow \begin{array}{l} C_{17}H_{35}COONa \\ C_{17}H_{35}COONa \\ C_{17}H_{35}COONa \end{array} + \begin{array}{c} CH_2OH \\ CHOH \\ CH_2OH \end{array}$$

Glyceryl stearate in tallow — Caustic soda — Sodium stearate or soap — Glycerine

In the above equation it is not necessary to use a stearate but any fatty acid or oil may be substituted, but no matter what the fat, it requires and alkali for saponification and all act in a manner similar to that above. However when rosin is used the action is somewhat modified as rosin is an acid and unites directly with the alkali to make a salt.

As soap is used for a great variety of purposes, its preparation of course varies. If a high grade soap is to be made the material used must be of the best, but if a cheap soap is to be manufactured then lower grades of fats and oils can be used quite as well.

The soap stock tallow or oil is received by soap--makers in terces or drums from which it must be melted out for bulk storage. This is done in a melting out or steaming out room. The room is usually built of wood with an iron sheathing and a floor of iron plates. The floor slopes fsom the back to the front so that it is drained out and no products can accumulate. The room is divided into compartments which are just a little larggr in width than the drums. A light track is laid t through the center of each compartment so that the drums containint the tallow may be rolled in. A steam line for melting the fat runs through the middle of the track. At a distance equal to the periphery of the drum from bung to bung, a valve and short nipple with a swing joint is fastened to the steam line, the control of which is fastened to the outside of the room. A charge is set by rolling in the packages,blocking them and fitting the nipple with the valve open, into the bung hole. The steam is then turned on and the melted tallow or oil runs out to a trough or ditch in the front part of the room. As the melted tallow runs into the pipes leading to the storage tanks it is strained so that no large particles pass along with it. Each package as it comes from the room is examined for unmelted fat by means of a light on a cord which is dropped into the bung hole. The time required for melting out the fat varies with the fat and the surrounding temperature. In winter the time required is longer than in summer.

This melted tallow will always contain a large amount of water, from the dondensed steam and it is important that this be removed as soon as convenient. The tallow is carefully watched and weights checked, so that they know just what kind of stock they have on hand in each storage tank.

The storage-tanks are made of iron with loose fitting wooden covers and they may from time to time be removed and the tanks cleaned. Steam pipes or coils are laid in the bottom of the tanks to keep the fat above the solidifying point. The fat is now ready to be boiled and for this purpose large round or square iron kettles, heated by cols are used. The coils have small holes for the steam outlet and to keep the substance well stirred while boiling. Generally the kettles are surrounded by a jacket of insulating material to keep in the heat during the boiling of the fat. When the fat is pumped into this soap kettle along with if is pumped a stream of caustic soda lye. When these are well mixed a large amount of heat is generated by the action and then for a while the steam may be slowed down. From time to time during the process a small amount of soap is run out, rubbed between the fingers, and tasted. If a sharp taste is present, there is an excess of alkali. The excess of alkali or the alkalinity of soap is tested further as follows: a sample is obtained from the kettle and a small amount of salt is added to separate the lye. Ten cubic centimeter of the lye are then put into a graduate, three drops of phenolphthalein solution and N/8 sulfuric acid are added and the mixture shaken until the solution is decolorized. Each 2 cc. of acid used equals .10 per cent of alkali present. This process is repeated several times and if no excess or not enough alkali is present, more is added. Alkalinity of not over .20 per cent is very desirable and a kettle which holds this alkalinity after three boilings and tests may be considered as finished.

The soap is now ready to be separated from the free glycerine or as it is called, "graining". This is done either by shoveling into the kettle of boiled soap dry salt, or running in a saturated brine solution which precipitates the soap as a curd. This rises to the top and the glycerine solution settles to the bottom and is drained off. The soap is then boiled up and if itiis thick a little water is run in and the soap is boiled until it forms a thin smooth substance. The steam is shut off and the soap allowed to stand for a week to settle. The soap separates in layers, the good soap (that is that containing a small amount of free alkali) is the upper layer. The lower layer contains about 55-70 pre cent of water, free alkali and any other alkaline impurities such as sodium sulphate and sodium chloride.

The soap is now pumped out of the kettle into the "crutcher" or mixing machine. The word crutcher is used because in the old method of making soap the soap was stirred with a wooden stick the shape of a crutch. If any filling is used it is put in at this stage. Some of the fillers used ~~was~~ in laundry soaps are sodium carbonate, sodium silicate, borax, starch, talc, grit or perfume. These fillers are considered as adulterations but are not harmful in the soap. When the soap is thoroughlly mixed and is in a semi-liquid state it is dropped out of the bottom of the crutcher into frames. These frames are tight boxes supported on a truck and they hold the contents of one crutcher. When the soap is hard enough the sides of the frame is removed (called stripping the soap) The soap is left in the frame generally three days in winter and four days in summer. It should be stripped, however, as soon as possible, for the soap should be cut when cool. Before the soap is cut into cakes it goes through a "slabber" which is a machine for cutting the soap into slabs the size of the frame. From the cutting machine the soap falls onto a rack in which it is carried to the drying--room. When the surface of the cakes dries over then they go to the wrapping room where they are wrapped by machinery.

CLASSIFICATION OF THE SOAPS.

A great variety of soaps are known, the appearance and properties of which vary according to the method of manufacture. The methods of manufacture may be classified as follows: (1) Boiling the fats in open vessels with indefinite quantities of alkaline lyes until products with definite properties are obtained. These products may be divided into several classes (a) The soft soaps in which the glycerine is retained. They are usually potash soaps of linseed oil or olein. These soaps do not dry when exposed to the air but rather absorb water remaining constantly like a jelly. As a rule these soaps are impure solutions of potassium oleate in an excess of potash-lye mixed with the glycerine separated in the saponification. Soft soaps can be prepared only with potash lyes although in practice, one part of soda is substituted for a part of the potash to assist in hardening the soap. There is no separation of the soap from the under-lye, which contains all the impurities, consequently these are all found in the soap.

In consequence of the solubility and cleansing properties of the soft soap, its use is preferred to that of soda soap in the manufacture of cloth and woolen articles. The fats used in soft soaps are mixtures of the vegetable and animals oils, as the fish oil known as "Southern," with rape, hemp and linseed oils. The particular oil used varies with the time of year and the market price; in winter soft oils such as linseed oil and olein are employed; in summer the firmer oils such as cotton-seed oil, colza, sesame, palm, or fish oil. Drying oils are preferably used. The soft soaps of different countries vary according to the oil most cheaply and easily obtained . In England, whale, seal, and linseed oils are chiefly used. In continental Europe hemp-seed, linseed, rape-seed, poppy and train oils, while in the United States, cotton-seed oil and oleic acid are employed.

"Summer soap" as it is called contains, owing to the fat emloyed, more potassium palmitate in proportion to oleate than the winter soap. Some of these soaps are transparent (plain or variegated), others opaque and white or yellowish. The best soft soap is made from hemp-seed oil, this oil imparts a green tinge to the soap which however can be imitated by adding indigo to some of the inferior soaps. Soft soap is generally used for fulling and scouring, but abroad it is sometimes used for washing linen, to which it imparts a most disagreeable fishy odor which is almost impossible to conceal by any amount of perfume.

The boiling of the soft soap commences with a strong lye containing from eight to ten per cent. potash, by which an emulsion is formed. The scum is dashed about with a beating-stick, and by this means all the alkali is taken up. A fresh lye is then added and the boiling continued until the soap upon cooling stiffens into a clear tough mass. When the soap contains too much caustic alkali, which can be ascertained by the taste, more oil is added. "The clear boiling" now commences during which the excess of water is removed. To avoid a long evaporation concentrated lye is employed and the soap instead of bubbling up has its surface covered with blisters as long as the hand, which are called leaves. When the boiling is finished, determined by placing some of the soap to cool on a glass plate from which if firm it can be separated the soap is cooled and stored in barrels.

Soft soap will take up a considerable quantity of water-glass solution without alteration. Recently for fulling there has been added to the soft soap a solution of potassium sulfate or a mixture of alum and common salt and also potato starch.

Liquid soaps are only another class of soft soaps to which glycerine or alcohol has been added.

(b) "Hydrated" soaps or filled soaps are prepared with sodium hydroxide as the base, and as in the case of soft soaps the glycerine is retained. Fatty matter and soda are run into the kettle and are boiled together. Care is taken to avoid an excess of alkali at first. When the saponification has taken place lye is cautiously added until the soap has a faint alkali taste, when it is ready to be transferred to the frames without any salting out or separating of the mixture, but the entire contents are sold as soaps. On cooling the whole solifdifies and does not betray its proportion of water.

This property of appearing dry and hard, along with a heavy precentage of water is a peculiarity of coco-nut oil soaps, which communinicate the same property to tallow and palm oil soaps. A yield of 200 to 300 kilos of fat is not uncommon, especially if water-glass is used.

Marine soap is a soap of this type. It is so called because it may be used with sea-water. It is entirely a coco-nut oil soap.

(c) True hard soaps which still constitute the great bulk of those made in England and the United States, requires more care in making than those varities just mentioned. Castile, curd, mottled, yellow and transparent soaps are all types of hard soaps and are soaps which are the most familiar to us.

The German tallow or curd soap is essentially a mixture of sodium stearate and palmitate. It was formerly prepared indirectly by first saponifying the tallow by means of caustic potash, and then converting the potassium stearate and palmitate thus formed into the corresponding sodium compound by adding common salt.

The soap boiling pan employed is somewhat conical in shape. It is made of cast iron and provided at the top with a high lintel or bulwark to prevent any fluid boiling over. Into the cauldron is first poured about 500 liters of strong lye at 20 per cent (sp. gr. 1.226), next the tallow is added and a wooden or iron lid having been fitted to the cauldron, the fire is kindled. When the mixture boils, it is kept so for five consecutive hours, and the contents are stirred constantly. The materials in the cauldron are converted into a soap-glue, as it is termed, a gelatinous mass, which if the operation has been carried out carefully, ought not to become thin when more lye is added. It does not many to be so thin that it flows in drops but should treacle from a spatula. This consistency may be produced if oil of tallow is added to the lye gradually and in small portions at a time.

¶ Knapp in his researches, found that it is always advantageous to first convert the fat with the required quantity of lye, into an emulsion, and to leave the lye either not heated at all or only to 50° in contact with the fat, so as to saponify first slowly in the old and to finish off with ebullition. When the saponification is complete the operation of "parting" is proceeded with and consists in adding from 12 to 16 pounds of salt to 100 of tallow. The soap is kept boiling until the soap-glue has become a greyish mass, from which the mother liquor or under-lye readily separates, the latter being let off by a tap; or if no tap is fitted to the cauldron the soap which is a curd on the top, is ladled over into the cooling tand. The salt added not only aids in separating the soap from the lye but also converts the potassium into a sodium soap. If the soap-glue has been removed it is again put into the cauldron and a moderately strong lye added, and heat again applied. The soap again becomes quite fluid, but consists chiefly of soda soap-glue. The boiling is kept up and during its continuance fresh lye and salt are added alternately. By continued boiling the soapy mass becomes ore and more concentrated; as soon as the foaming ceases and the whole ass is in a steady ebullition, it is again ladled over into the cooling tanks or the mother liquor is tapped off. The object of this second boiling is to convert the material into a uniform mass free from air bubbles, this is done by beating with iron rods. The hot soap is next placed in a wooden box, cooled, cut into bars and placed in a cool dry room.

A soap closely resembling the curd soap in its preparation is the 'mottled' or olive oil soap. The kind of soap is the Marseilles, Venetian or Castilian soap and is chiefly prepared in the southern parts of Europe. Olive oil used is frequently mixed with other kinds of oils such as linseed, poppy seed or cotten-seed oil. Two kinds of lye are employed in the preparation of this soap, the first lye is a caustic soda solution for "fitting" or preparatory boiling; the other lye is mixed with common salt and used to separate the soap. The preparatory boiling is principally to form an emulsion so that the contact of oil and alkali is greatly promoted and forms a real soap-glue. In order to remove the water from this material as much as possible, a lye containing common salt is employed, and lastly by a third boiling the saponification is completed. By the use of the lye containing common salt, it is possible to keep the soap-glue in such a condition that it can take up alkali without combining with the water. The preparatory boiling is carried on in large copper vessels, capable of containing 250 cwts., the caustic soda employed for this purpose having a strength of from 8.2° to 12.5° Tw.(sp.gr. 1.064) The lye is brought to boiling first and oil to be saponified is next added, care being taken to stir the mexture in order to promote the reaction. Gradually the mass becomes thick, and as soon as black vapours arise, due to the decomposition of a small quantity of the soap-glue coming in contact with the hot copper, there is added the stronger lye of 30° TW.(sp.gr.1.157). If a blue-white soap is to be produced in iron sulfate is added, when the soap has the consistency that when it solidifies the coloring matter added will settle in veins or are deposited to give the mottled appearance. In the old-fashioned type of Castile and Marsilles soap this mottling would not take place if the proportion of water exceeded a certain limit, because the soap was so fluid that the coloring matter entirely settled to the bottom, so it was generally considered a good soap free from a large amount of water if it had a mottled appearance. In late years however, it has been found that the mottling can be brought about in soap heavily watered by adopting certain methods of manipulation, for example, adding a certain proportion of silicate which thickens the texture, and stirring the soap while cooling, until the mass becomes stiff enough to prevent separation of coloring matter. If other solid fats are used with olive oil the consistency required for mottling can be obtained with as much as 50 per cent. of water with coco-nut, and palm oils, mottled soaps can be prepared containing 70 per cent. or even more of water, in addition to an increased amount of alkali. These soaps however should not contain more than 2 per cent of sodium carbonate and less than ten per cent. of disolved salts, otherwise the soap will effloresce on drying, provided it is sufficiently stiff to permit of mottling. So that the mottled soap of modern make and that of the older type are by no means the same thing in composition and quality.

A good sample of Marseilles mottled soap should contain:

	(1)	(2)
Fatty acids	63	62
Alkali	13	11
Water	24	27
	100	100

A type of mottled soap which is often prepared with a yield of 180 to 200 per cent. is that made with almost equal quantities of olive oil and coco-nut or palm oil. In this case the manufacture of th theolive oil soap is carried out separately, as far as the stage where it is separated from the lye, so as to remove the impurities. It is then introduced into the pan where the coco-nut oil has been saponified in the hot with caustic soda of about 20° Bé., together with s some 13 per cent. of sodium carbonate dissolved in the water. Unger in 1869 found that in order to prevent coco-nut or palm oil soap from drying, it should not contain more than 43 per cent of soduim carbone ate, calculated on the weight of coco-nut oil or one mol. of sodium carbonate to every four mols. of pure coco-nut oil soap. When these two soaps have mixed they are boiled and 4 to 5 per cent.(that is of the totla fat) of sodium chloride solution of 24° Bé. is gradually added, the substance is then heared until the paste boils readily without sticking to the sides of the copper, and the steam evolved produces at the surface of the soap crevices in the form of resettes. The soap will then emit a hollow sound and will not form bubbles when hit with the stirrer from which it falls inbbroad folds which are covered with a dry skin; when put on a glass it is covered with a film or becomes coated over the top while beneath it remains fused and when pulled between the fingers it tends to solidify.. It is very important that it shoild not contain an excess of caustic soda or not more than 0.2 to 0.3 percent and is best it is neutral. The excess of alkali present may be eliminated by adding the calulated amount of coconut oil or hydrochloric acid determined by titration. At this stage the coloring matter is mixed in and the soap is then cooled to 75° and poured into large solidifying frames so as to cool slowly, in winter the frames are wrapped with cloths, so that the mottling may be satisfactory. The mottled soaps which have a high yield of about 400 percent are given the name of blue mottled or "Eschweg" soaps, and were largely used some years ago. Even now they are used extensively for several reasons: First, they have a higher detergent power than the finished soaps, because they contain allarge amount of alkali carbonates; secondly, they dry more rapidly than the resin soaps; and thirdly, they are harder and thus are preferred for laundry purposes as there is no waste even when the clothes are vigorously rubbed.

Yellow soaps or palm-oil soap are made in large quantities. Crude palm oil is employed in the manufacture of the common kinds of yellow soap. The same oil is used in some white soaps, it is then bleached with potassium dichromate and sulfuric acid. Another kind of yellow soap is resin soap, and will be considered under that head.

(2) In the second method the fats are acted upon by the exact quantity of alkali necessary for saponification, without the separation of any waste liquor, the glycerine is retained in the soap. This includes (a) Soaps made by the cold process and (b) soap made under pressure.

(a) The so-called "cold-process" requires the exact weights of well refined fats and caustic soda of a given specific gravity, the quantities are such that only just enough soda is present to completely saponify the fat. In the manufacture of toilet soaps by perfumers and manufacturers who work on a comparatively small scale, "cold-processes" have long been in use. They use this process because of the simplicity of the apparatus, a pan and some agitating appliances are the only necessary equipment. The products are sometimes referred to as "little pan soaps." The mixture of oils and fats to be saponified are first made fluid by a gentle heat and is then mixed thoroughly with the appropriate quantity of alkali, of necessary strength, which has also been previously warmed to a temperature usually considerably below the boiling point. The mass is then well covered up to keep in the heat and set aside for some time. Usually the saponification does not take place very rapidly and it is some time before the mass begins to increase in temperature due to the heat generated when the chemical change takes place. When perfumed soap is thus made the process is carried out at as low a temperature as possible, in order to avoid any in jury to the scent apt to be caused by long exposure to higher degrees of heat.

Toilet soaps are also made by other processes, such as remelting the raw soap and then adding perfume and coloring; by cutting odorless soap into fine shreds by a machine, adding perfumery, coloring and other ingredients as vaseline and lanolin. The soap is then passed between rollers, the sheets or bars thus formed being cut into tablets. This process is called "milling" and was first carried out in France. The best toilet soaps are made by this process. There are two great advantages of this method: first since no artificial heat is applied very delicate flower perfume may be added to the soap mass which could not be used with a re-melted soap because the heat would destroy the odiferous matter. Secondly, as the resulting tablets usually contain only a small quantity of water a given weight of soap-cake usually contains a much larger quantity of actual soap than another cake of the same weight prepared by remelting or by cold process, besides being harder and stiffer it lasts longer, wasting less rapidly during use. Another process consists in scenting and coloring pure white common soap without any intervening cooling. The coloring materials used in toilet soaps must be colors which are not effected by the alkali. Aniline colors are not used because they are so sensitive to light. The azodyes are the more suitable for soaps and eosin colors are used principally for transparent soaps. For opaque soaps mineral red is used. Vermilion is used but it is expensive so iron oxide is used in the cheaper soaps. To give a violet color the tar colors for violet are used; for blue ultramarine and indigo; for yellow saffron, tumeric, picric acid and naphthol yellow; for green, blue and yellow colors are mixed; for black or/gray lamp black; for brown a solution of raw sugar or caramel. Some of the perfumes used to scent the soaps are cumin oil, bergamot oil, oil of lavender, oil or thyme, oil of roses and gilliflower water. The soaps adapted for generl or laundry purposes contain some alkali in excess but one important requirement for toilet soap is that they shall not contain any free alkali. Some dermatoligists even demand that there shall always be some unsaponified fat, otherwise the soap has an irritating effect upon the skin.

Transparent soaps made by the "cold process" often contain free a alkali as well as unsaponified fatty matter because the saponification is not always complete. A sugar solution is added to the soap to make it clear and when this is used, free alkali must be present to pervent muddiness. Such soaps are often of the vilest quality imagineable and are confounded with the older type of transparent soaps prepared by dissolving dried soap in a good quality of alcohol.

(B) In order to avoid in complete saponification so liable to be produced by the "cold process" another method has been introduced employing a higher temperature and an increased pressure. The object of this is to shorten the time required for open boiling. Autoclaves or pressure boilers are used for this process.

Resin soaps are now made in large quantities and by almost all manufacturers. Colophony and ordinary fir-tree resin combine at boiling heat more readily with alkalies than do fats and oils but the compounds obtained by heating resins alone with alkalies are not true soaps in a chemical sense nor have they the appearance and properties of true soaps. When tallow is saponified along with a portion of resin a true soap is obtained.

Colophony contains acids which behave like the fatty acids and yield similiar soaps which lather well in water, and may be mixed with ordinary soap fat and make the soap much cheaper. Fats which contain acids are more readily saponified than perfectly neutral fats, olive oil and tallow. This applies to resin which consists essentially of a peculiar acid, but in these instances no real saponification takes place, in as much as no glycerine is formed.

The saponification of the resin is effected with a strong lye solution to avoid excessive frothing. It is necessary to employ pure fats and pure resin (with saponification number 160 to 180) and when saponification is complete, the soap must be well "finished" in order to avoid excess of alkali which would cause efflorescence.

The resin may be introduced as a powder directly into the fused fat, but it is more generally added after the fats have been saponified and the soap salted out and separated out from the lye. The concentrated caustic soda is then added and the resin gradually disintegrated by heating and stirring. Boiling is continued until the froth almost disappears and the soapy mass separated from the under-lye and exhibits the proper consistency when pressed between the fingers.

Good resin soaps hould not contain more than 40 percent of resin but in some cases they show as much as 100 percent (compared with the fat) and it is a question whether resin soap should be regarded as adultersated. Of course the manufacturers object to this, for obvious reasons. Although attempts have been made at various congresses to fix limits of 10, 20, or 30 percent of resin allowable but none of these have been regarded. The only way to solve the case would be to have the manufacturers stamp on every cake of soap the resin content and then there would be no question of adulteration or fraud.

METALLIC SOAPS

By adding soluble salts of the heavy metals to a neutral soap solution a percipitate of metallic soap is obtained. These soaps are insoluble in water because they do not have as their base potassium or sodium. Some of these metallic soaps have a very extensive application in the industmies and in pharmacy. Some of the most important metallic soaps and their use will be taken up.

One great industrial use for metallic soaps is as a drier in paints and varnishes. Manganese, sinc and lead soaps are used extensively for this purpose especially when the oil is linseed. Manganese soap is obtained by decomposing manganese sulfate with common soap or by dissolving manganese carbonate in oleic acid. Lead soap may be formed by double decomposition or by saponifying litharge or white lead with olive oil. It is a yellowish white mass.

One important property of a varnish is that it must harden or dry in a short time. The hardening of varnish is due to oxidation and some varnishes or japans are oxidized rapidly by increasing the temperature, such varnishes are called baking japans. In other varnishes oxidation is brought about by the use of driers. These varnishes are composed of linoleates or resinates of lead or amnganese, usually containing free oil and often some resinous or oleoresinous varnish and dissolved to a thin liquid with turpentine or benzine. These are called driers and they act by catalysis and cause rapid oxidation of the oil or varnish to which they are added. It is well known that lead and manganese form two classes of compounds--a protoxid and a peroxid; and readily pass from one to the other. If they are present in the film in the higher state of oxidation they give up half their oxygen to the oil, then take up more from the air and so act continuously as agents to pass along oxygen from the air to the oil. Manganese is more active than lead but each has its advantages. Driers may be made with other metals such as nickel and cobalt which rapidly pass from one state of oxidation to another, but have no special advantages over lead and manganese. These compounds may be made by directly heating the metallic oxides with oil or resin, or by decomposing soaps with soluble salts of these metals. If we introduce into the oil and amount of metallic soap equal to even one thousandth of the weight of the metal, the effect is very marked.

The use of too much drier is objectionabe since it is likely to continue to act, slowly of course, after the film has hardened, and in time destroy its elasticity and coherence. Driers are not generally used in spirit varnishes nor baking-japans. A mixed copper and iron soap, obtained by precipitating with soap a mixed solution of copper and iron, if ground up with litharge varnish and wax serves to produce a permanent green bronze on plaster figures.

In paints the same metallic soaps are used because they dry rapidly and give a gloss to the paint if added when oil is heated to a very high temperature.

The various greases on the market may be divided into four main groups according to their chemical, physical and mechanical composition.

(1) Greases with alkali soaps used as hardeners or solidifiers.
(2) Greases made with fatty oil and lime soaps.
(3) Greases made both with alkali and lime soaps.
(4) Greases made with rosin oil and lime soaps.

The greases in the above classes vary greatly in composition and in the kind, quality and percentages of the various ingredients entering into the compounds. They may contain anywhere from four or five pereent up to fifty or sixty percent of soap and by carefully choosing the materials the soaps, and the fillers, and by varying the proportions, greases can be made in any desired consistency.

Besides the alkali and lime soaps, zinc, aluminum, magnesium and lead soaps are used as ingredients of greases and lubricating oils. There is a class of lubricants known as lead soap lubricants. Lead soaps are hard at low temperatures, viscous at ordinary temperatures but sufficiently fluid on heating by friction. The melting points of lubricants prepared from these substances is high and they are therefore less suited to high speeds. Lead soaps make a class of lubricants known as "anti-friction lubricants".

Lubricants made with ordinary soft soap is serviceable for some purposes but it is liable to contain a part of the alkali unfixed by which damage would be done to the metals.

There are several methods by which cloth may be rendered waterproof. Cotton and linen may be rendered waterproof by using gum or gelatine containing one tenth to one fiftieth percent of potassium bicarbonate and then exposed to the sunlight. The gelatin becomes insoluble and remains firmly fixed to the cloth.

Aluminum soap has also been used but when cloth is waterproofed by this method, I found that the soap was precipitated within the cloth and not applied to it as aluminum soap solution. The cloth to be rendered waterproof was first passed through a solution of aluminum sulfate dissolved in cold water and then through the soap solution. This gives rise to the formation on the cloth of an alum soap. This same principle is employed for coating metallic surfaces which have to with stand considerable heat. The metal is dipped in soap solution and then precipitated by alum solution.

Cement is rendered waterproof by adding alum to the cement before mixing the cement and then treating this mixture with soap solution and thus the aluminum soap is precipitated within the cement rendering it waterproof. Alum thus added in powdered form to the cement accelerated the setting of the cement. Using ten and twenty percent soft soap solutions the set was accelerated and increased directly as the percent of soap present. The addition of alum and soap in some cases gave higher strength tests especially so with coarse cement. The permeability also was reduced.(1)

Metallic resin soaps may be produced by double decomposition of potassium hydroxide resin soaps and a soluble metallic salt. From these good varnishes are obtained and such soaps are used to render paper and carriage covers waterproof.

There are several kinds of soap preparations which are used as disfectants and in pharmacy. Among these may be mentioned the cresol, carbolized, naphtha and formaldehyde soaps.

The naphtha soap was made with alkali metals and naphthalic acids. The following will show the disinfecting power of this soap: The cholera vibris when exposed in less than three percent of the soap were killed in three hours; six percent killed typhiod and four percent killed staphlococcus.(2) Formaldehyde and resin soap is said to be superior in germicidal value to the other saponaceous disinfectants.

There does not seem to be much difference in the disinfecting power of ordinary and carbolized soap. The disinfedting power is not determened

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(1) Chemical Abstracts 1912 Vol. 6 Part1, page 282 Influence of soap and alum on cement.

(2) Disinfecting power of naphtha soap Dzevagoviskii and Stepanova Arch. Sci. biol. 14, 283-303

by free alkali present and the phenol soaps which contained not free alkali are superior to those which have alkali in excess.

There is a metallic soap however which is very effective as a disinfectant and that is a mercury soap prepared by mixing soaps with an alkaline salt of a complex mercury substituted carboxylic acids of the aliphatic or aromatic series. The organic compounds of mercury are much to be preferred to the inorganic as they are no injurious.

A colloidal copper soap spray is perpared by dissolving 500 grams of copper sulfate in 50 liters of water. Dissolving 2 kilograms of soap free from alkali in 50 lithers of water. The copper solution is then stirred in the soap solution. It is best to use rain water in making up the solutions and the soap should consist largely of sodium oleate containing a little sodium stearate to prevent colloidal solution. The spray is a bluish green opaque liquid of constant low surface tension. If it is centrifuged for several hours or allowed to stand for five months no sediment was perceptible. (2)

Dr. H. I. Jones and Robert Du Bois discovered that aluminum soap precipitated from a solution of ordinary soap by a solution of alum was soluble in gasoline. This solution is an excellent preservative for eggs. The eggs are dipped into sulfuric acid and then into the soap solution. When treated in this manner, the eggs could be preservdd for many months and to all appearances were just as fresh as when first treated.

(2) Vermorel and Dantony. Compt. rend. 152, 1263-5

A medicine for use in the treatment of anemia is formed of iron stearate or other iron soaps dissolved in stearic acid or other soap forming acid. Calcium soaps are similiarly perpared for use as a medicament.

A large number of fabrics which had deteriorated in laundering were examined. It was discovered that metallic soaps had been deposited on or in the material and caused the material to rot as they acted as an ozygen carrier.(1) This brings out the importance of using water and soap free from metallic salts especially iron salts.

Arsenic soaps composed of potassium arsenite, soap and camphor have long been employed by taxidermists for preservation of skins of birds and mammals.

Sodium arsenite is used for preventing incrustations in steam boilers.

A compound known as "lead plaster" is prepared from olive oil and lead oxide, and is known as porous plaster. It is especially used as a carrier of substances with medicinal proporties. Used greatly in medicines or as medicines.

SOLUBILITY OF METALLIC SOAPS

The sodium and potassium soaps of almost any oil or fat are readily soluble in cold and hot water and alchol, but the soaps of the heavy metals are characterized by their insolubility in water. There is no one hydrocarbon solvent in which the soaps of the heavy metals seem to be soluble, but the solvent varies with the metal.

(1) C.A. Mitchell. Mat. Grasses--3100-1. Action of metallic soaps in Laundering.

Lead soap with linoleic acid goes almost completely out of solution from all petroleum solvents in less than one hour. The nickle el soaps separate out in several days. The iron soaps go into solution and increase in weight (due to oxidation).

Aluminum soap is soluble in benzine, oil of turpentine and gasoline.

The oleates of calcium, magnesium and iron dissolve in glycerol. Ammonium oleate is readily soluble in water. Barium is insoluble in water, and difficulty soluble in boiling alchol. Magnesium is soluble in alchol and petroleum spirit. Cupric oleate dissolves with a green color in all proportions of alchol, ether and fixed oils. Lead is soluble in alchol and ether, especially when hot. Zinc is soluble in carbon bisulfide and petolium spirit.

ANALYSIS OF SOAP

There are certain characteristics a soap must have in order that it may be classified with the best grade of soaps. They are as follows:

(1) Greasiness to the touch.

(2) Must be readily soluble in water, forming a viscid solution which on agitation yields a tenacious froth or lather.

(3) It must not crystallise out.

(4) Readiness to amalgamate with small proportion of hot water, into a homogenous substance which on cooling sets into a jelly or paste.

(5) Must give an alkaline reaction.

(6) Must have an acrid taste.

(7) There must be no ddor of the oil used.

All soaps do not contain these necessary properties, and some are highly adulterated with water, silicates, talc, and often times harmful impurities. The adulterations and the true composition of soap may be determined by analysis.

First the estimation of the amoun of water present is important. There are many methods for determining this. One very simple method is to cut the soap to be tested into shavings, weigh out a definite amount and expose to the temperature of 40° or 50°C. care being taken not to melt the soap. When dry reweigh and the loss in weight is the amount of water that was present in the sample.

The best method was devised by R. M. Fitzpatrick, and is as follows: In a 200 cc. conical flask one gram of sample is weighed and warmed until the soap is dfsolved. The solution after codling is filtered into a 20 cc. of absolute alchol. The paper and residue are dried and weighed/ The filtrate is allowed to cool and 5 grams of anhydrous sodium sulfate added. The flask is stoppered and allowed to stand for twelve hours. Solution is then filtered into a weighed conk al flask. The sodium sulfate in the flask and on the filter is washed with warm absoute alchol. The alchol is evaporated on a water-bath, and the soap dried fifteen minutes in a steam oven, then codled and weighed. This weight and the weight of alchol insoluble residue subtracted from the weight of the soap taken gives the weight of water. A necessary po point to observe is that the solution before adding sodium sulfate does not deposit any soap jelly.(1)

The proportion of water in soap varies greatly. In the so-called "dry soaps", and in some of the best kind of curd soap it does not exceed 16 to 20 percent, while in inferior soaps made from cocoanut oil it sometimes reaches 70 to 80 percent.

By treating the dry soap with petroleum spirit unsaponified fats or free fatty acids are dissolved. Insignificant proportions of unsaponifiable matter neutral to fixed oils may also be found in the the petroleum spirit, and nitro-benzene and essential oils used for scenting the soap will abso be dissolved. The residue from medicated soaps may also contain metallic oleates and free carbolic and cresylic acids, thymol and hydrocarbons such as vaseline and other neutral petroleum and tar products. If the solution containing these substances be evaporated down and the residue indicates the desirability of further examining it then tests for heavy metals, fatty acids and unsaponified fats may be made.

The portion of the sample not volatile at 100° and insoluble in petroleum spirit really constitutes the soap proper. An aqueous solution of the soap is then made and the solution is decomposed by normal sulfuric acid. Nitric acid is preferred by some because it enables one to determine the sulfates by barium chloride in one portion of the

(1) "Estimation of Water in Soap". Vol. 6, Pt. 1. Chemical Abstracts, 1912 pg 432. R. M. Fitzpatrick.

filtrate and chlorides by silver nitrate in another.

The method of separating the oily layer of fatty acids from the aqueous liquid depends on circumstances.

When the soap is chiefly a stearate of palmitate, as that made from tallow or palm oil, the liberated fatty acids are solid when cold, and in such cases there is no better plan than to precipitate them and weigh.

If fatty acids are liquids at ordinary temperatures or form a cake deficient in consistency, a known weight of dry bleached beeswax or stearic acid may be added to the hot liquid. The fatty acids become amalgamted with the melted wax, and on cooling a firm coherent cake is formed which may be at once wiped and weighed. The weight of wax added being deducted from that of the cake, the weight of the crude fatty acids is at found.

The solution separated from the fatty acids when neutralized with standard alkali will of course be alkali--sulfates. In addition it may contain sodium chloride, soluble fatty acids, glycerol, sugar, dextrin, starch, gelatine and other matters. For the detection of these it is necessary to work on separate aliquot portions of the solution.

The sodium chloride may be determined by titration with decinormal silver nitrate or deduced from the weight of the silver chloride precipitate.

Soluble fatty acids rarely require determination in soap. However they may be determined by titrating with standard alkali solution using phenolphthalein as an indicator.

Glycerol may exist in soap in variable amounts. In the absence of sugar it may be determined with considerable accuracy by the permanganate method. When glycerol is present in considerable amount in soap, Lewkowitsch makes the determination by dissolving it in water, separating the fatty matter with acid, and filtering off. The filtrate is then neutralized with barium carbonate and boiled down to the consistency of syrup. The residue is then extracted with a mixture of three parts of 95 percent alchol and one part ether, the alcholic solution filtered and evaporated on the water-bath to small bulk, and finally dried under a dessicator. The glycerol in the residue may be determined by the acetin method. The presence of sugar renders the above method wholly useless, and one of the plans described below must be adopted.

Sugar is rarely present in transparent toilet soaps, but in these it sometimes exists to the extent of 20 to 30 percent of the entire weight, or in a proportion approaching that of the anhydrous soap present. Such soap is sometimes sold as glycerine soap, though wholly destitute of glycerol.(1) According to Donath and Mayrhofer(2) the determination of sugar and glycerol may be made by addin to the solution slaked lime sufficient to combine with the sugar and an equal quantity of washed and ignited sand, boiling down to the consistency of syrup, pulverising the cooled residue and exhausting it in a closed vessel with 80 to 100 cc. of a mixture of equal parts of ether and alchol. The glycerol will pass into solution, and after cautious evaporation of the solvent, may be determined by the acetin or oxidation process.

Sugar may be determined by Fehling's solution after inversion without previously separating the glycerol but the solution should be dilute and the boiling very limited in duration, or the glycerol will probably cause some reduction.

To determine the alkali in soap a method devised by C. Hope is used. It is as follows: Two grams of the soap are dissolved in hot absolute alchol, a drop of phenolphthalein solution added, and carbon dioxide passed in till any pink coloration is destroyed. The liquid is then filtered, the residue consisting of total impurities, washed with hot alchol, weighed and then titrated with decinormal acid and methyl-orange to find the alkali not existing as soap. The alcholic solution is evaporated to dryness at 100°, and the residue of dry soap weighed when constant. It is then ignited gently, treated with water, and the solution titrated with decinormal acid and methyl-orange to find the alkali existing as soap. The difference between this and the total residue before ignition gives the fatty anhydrides whidh multiplied by 1.03 gives the fatty acids.

Organic matter, such as starch, dextrin gelatin and so forth may be detected by special tests, but their recognition is more easy and certain if tested in the matter insoluble in alchol.

After drying and weighing the residue obtained at this stage a

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(1) A. H. Allen, Commercial Organic Analysis Vol 2-ptl. pp 288-89
(2) Quit. f. Anal. Chemis

minute quantity of it may be examined under the microscope by which many substances will be revealed by their characteristic structure. Iodine solution will color starch granules blue and render them more distinct. Gelatin is tested for by means of tannin. If gelatine be found, it is best determined by treating another quantity of the soap with strong alcohol and applying the Kjeldahl method to the residue. Gelatine contains about 17.9 percent of nitrogen.

The other part of the aqueous solution of the residue insoluble in alcohol should be rendered distinctly acid with hydrochloric acid and evaporated. A slip of tumaric paper should be immersed in the liquid towards the end of the operation and allowed to remain until the evaporation is complete. If a borate be present the paper will become brownish-red in color, and will be changed to green, blue, violet or black on addition of caustic soda solution. The residue is treated with hydrochloric acid, water added and the solution filtered. The residue of silicia is washed, dried, ignited and weighed.

There may then be some residue which has not been dissolved by petroleum spirit, alcohol and water. It is not always necessary to test for this depending of course upon the amount and the nature of it. In this residue is likely to be found insoluble organic matters, such as saw-dust, bran and woody fiber from oatmeal, mineral pigments and coloring matters, as red ochre, burnt umber, red lead vermillion, Scheele's green, chrome green and ultramarine; mineral matters such as scourers, sand, powdered quartz, pumice and infusorial earth; mineral matters such as adulterants or "fillings", china, clay, barium sulfate, chalk and whiting.

EXPERIMENTAL

Before preparing metallic soaps for study, soaps using potassium hydroxide and different oils and acids were made. These soaps were either pure oleic acid or cottonseed oil soaps, no mixture of oils were used as the commercially prepared soaps would serve that purpose just as well. These pure soaps were prepared so as to have some standard soap with which to compare the properties of the various metallic soaps precipitated from commercial soaps. After comparing the metallic soaps precipitated from pure soap solutions and those from some of the commercial soaps it was found that the commercially prepared soap solutions could be used just as well as the pure oleic and palmitic acid soaps. Ivory and Castile soaps were decided upon as the best from which to prepare the metallic soaps for study.

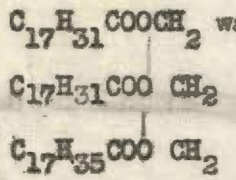
First soap using pure stearic acid and potassium hydroxide was prepared. The formula for stearic acid is $H\,C_{18}\,H_{35}\;O_2$ and its molecular weight is 284 grams. At first it was intended to use an amount of stearic acid equal to its molecular weight but since its molecular weight was so high only one tenth of its weight was used and also one tenth of the molecular weight of potassium hydroxide or 5.61 grams. The potassium hydroxide was dissolved in the least amount of alcohol possible before being added to the stearic acid. The mixture of acid and potassium hydroxide was then heated until completely saponified. It was found that more potassium hydroxide, was necessary to complete the saponification and so more was added until the soap had a sharp taste when finished. The final product was a pure white compound, not soft but firm and readily soluble in water and forming a good lather.

Potassium palmitate was next prepared. Coco-nut oil which is almost pure palmitin was used as the acid and potassium hydroxide as the base. Its formula is $C_3H_5(OC_{16}H_{31}O)_3$ and its molecular weight 807 grams. Of this only 20.15 grams were used as even only tenth of its molecular weight was too large an amount. As before an equal precent of the molecular weight of potassium hydroxide was weighed and dissolved in alcohol. The two were stirred together and heated until saponified. The heating was not carried out over a water bath so it was necessary to stir the contents of the kettle almost constantly to keep the soap from scorching. More potassium hydroxide had to be added before the acid would completely saponify. The soap formed was white but not such a clear white as the potassium stearate soap. In alcohol solution it appeared opaque and jelly like while the pot assium stearate was more solid and was simliar to vanishing cream. Potassium palmitate was readily soluble in water and formed a good lather.

Potassium oleate $C_{17}H_{33}COOH$ whose molecular weight is 282.3 grams was then used. One tenth of its molecular weight was weighed out and 5.61 grams of potassium hydroxide. The alcoholic solution of of potassium hydroxide was added to the acid and the mixture saponified. Potassium hydroxide being added as needed. The soap had a yellow color, was very soft, and when put in alcohol it made a brown solution which was quite different from the other two soaps but more like linseed oil soap.

Linseed oil or linoleic acid $C_{18}H_{32}O_2$and potassium hydroxide were saponified. Molecular weight of the acid is 252.2 grams but only 25.52 grams were mixed with 5.61 grams of potassium hydroxide in alcohol. Enough alkali was added until the soap had a sharp taste and was completely saponified. The potassium lineolate was a dark brown firm soap readily soluble in water. Its alcoholic solution was very dark, almost black and rather syrupy in appearance.

Cottonseed-oil $C_{17}H_{31}COOCH_2$ was next used and



$$\begin{array}{l} C_{17}H_{31}COOCH_2 \\ \quad\quad\quad\quad\quad | \\ C_{17}H_{31}COO\ CH_2 \\ \quad\quad\quad\quad\quad | \\ C_{17}H_{35}COO\ CH_2 \end{array}$$

its molecular weight being 878 only 292 grams were used. A larger amount was used compared with the others because this soap was to be used more for the experimental work which followed while the others were only to be used preparing standards. A large amount of potassium hydroxide was needed to completely saponify the soap. The soap was soft, but not liquid, of a consistency between a liquid and a jelly. This soap like the other soaps had a strong odor of the oil used in its preparation. The odor of oleic acid, linoleic acid and cotton seed oil soaps being very unpleasant. Cottonseed oil and sodium hydroxide in alcohol were also saponified but the soap when finished was dough like and rather stringy so the potassium hydroxide was used for e xpermental work.

In this place migh also be mentioned the ammonium and lithium soaps which were also prepared. In place of potassium hydroxide, ammonium hydroxide was substituted, alcohol and oleic acid were added to it and heated for some time. The soap was dark brown, smelt strongly of ammonia, and was an excellent detergent, of consistency of vaseline and readily soluble in water. Ammonium stearate at first was white and more crystalline. On standing several months the odor of ammonia disappeared and the soap took on a yellow tinge and became. brittle. When a piece was moistened and rubbed between the hands it did not lather.

Ammonium palmitate was pure white, and when rubbed on the palm of the hand felt smooth and soft. After standing for the same length of time as the oleate it still retained its white color except on the top where it had become quite yellow. It did not form a lather when put in a solution.

The failure to form a lather readily was one characteristic of these soaps yet they possessed detergent properties. One interesting fact noticed was that cottonseed oil and linseed oil with ammonium hydroxide failed to saponify and no soap could be made when the oil alone was used.

Lithium hydroxide (made by dissolving the metallic lithium in water) and palmitic were mixed and heated until saponification took place. The resulting compound had the appearance of yellow laundry soap and the consistency of thick cake dough. It did not lather readily in water but had cleansing properties. The high cost of lithium would be, the great disadvantage of its being used commercally in any way.

After having prepared these pure soaps for reference the commercilly prepared soaps were obtained and solutions made. Solutions of Ivory, Kirk's Flake White and pure Castile soaps were made and these solutions with the solution of soap prepared from cottonseed oil, were used in preparing the metallic soaps.

The metallic soaps using cotton seed oil were first made and studied. To a solution of the soap was added the various salt solutions of the metals. The first metallic soap was prepared by adding chromium nitrate to the solution of cottonseed oil soap. The soap formed on the top, but stuck together and in order to separate it from the under solution it had to be filtered. When first prepared it was a light green but on standing for a day or two it changed color and became dark and more brittle showing that the soap had oxidized as was true of all the metallic soaps from cotton seed oil when exposed to the air. The reason for the soaps becoming brittle is because oleic acid as well as linoleic acid is an unsaturated compound or as they are called "double bonded acids" and the double bond may open up and take on other elements in this case oxygen and then become saturated or a hard substance. This characteristic fact is made use of in using these as dryers. When metallic soaps are used for this purpose it should always be a soap from some unsaturated acid as oleic or linoleic but such is not always the case but metallic soaps from other oils and acids are used and then the hardening of varnish or paints is probably not due to the kind of soap present but more to the oil in the varnish.

In preparing the soaps, approximatily the same volume of soap solution was used but varying amounts of soaps were precipitated down, chromium gave a very small yield of metallic soap.

Zinc chloride was used to precipitate zinc soap it was a white soap, and the soap formed could not be taken off the top but had to be filtered in order to obtain it. The zinc soaps are used commercially in preparing salves and ointments as they are soft smooth soaps and when rubbed into the skin disappers similar to lanolin. Therefore zinc soaps from several acids were prepared. That from Ivory was pure white and powdery and too dry to be of any use as a salve. That from cottonseed oil and pure oleate naturally were almost identical, withe exception that the cottonseed soap was more yellow. Both were soft and vanished when rubbed into the skin evidently the zinc soap from ikeuc acud us tge the used in ointments and salves.

Iron sulphate precipitated the ferrous soap which had the characteristic color of iron and like the above soap had to be filtered in order to secure the soap as a mass. On standing it became dry and brittle and almost black in appearance.

Soap prepared with tin chloride was a white soap and formed a lump in the solution which could be removed without filtering.

Antimony chloride formed a fine white powdery soap which was difficult to collect even when filtered as it readily passed thru one filter paper.

Calcium soap was white and the yield was large. When exposed to the air it became hard and yellow and not readily soluble.

Arsenic chloride when added to soap solution came down as a sticky mass and the yield was so small that on standing a feq days there was scarcely enough to to save as a sample and several volumes had to be precipitated before enough soap was obtained to put in a small sample bottle. The reason for the small yield is that the soap is so soluble that it did not come out of solution as a precipitate.

When copper sulphate was used to precipitate the copper soap, the soap was formed as a hard mass and could be removed with the fingers an and excess of water squeezed out. When dry it was a very dark green and resembled crayon pencils.

Coppernitrate gave a lighter green soap which was powdery and had to be filtered to remove the water.

Lead nitrate seemed to give the best precipitate which was easily removed in a lump and the yield was fairly large. It was a white or yellowish woap.

Silver nitrat gave a good yield of a grayish soap which on standing became dark.

Nickel sulphate gave flaky light pale green soap which had to be filtered in order to be collected. When the soap was allowed to stand in the air for several days todry, it became brittle and dark green.

Cadmium nitrate added to soap solution formed the soap as a white lump on the stirring rod and in this way was removed. The yield was farily large.

Bismuth nitrate gave such a small yield of metallic soap that when it had stood a day or so in the air that it almost disappeared and similar to the arsenic soap several amounts had to made in order to obtain enough to het a good sample.

Mercury nitrate formed a soap which was a fine white powdery substance, which on standing became grayish black.

Cobalt nitrate formed a light pink soap which on standing become dark green and brittle. When put into solution it gave a pink color. Yield was very small.

Manganes sulphate gave a soap which formed a white lump on the stirring rod and which on standing became darker in color.

Barium and strontium soaps were similar to the calcium soap--were yellow and had the appearance of yellow laundry soap.

The ferric soap was a dark brick red which darkened on standing. A large amount of soap was formed from a relatively small amount of soap solution.

Magnesium chloride gave a white soft powdery soap.

The above soap with cottonseed oil all became dry and brittle on standing and many of them changed a great deal in appearance. It is from this class of soaps that the metallic soaps for diriers in paints and varnishes are obtained.

The same metallic salts were used to bring down the metallic soaps with Ivory and Castile soap solutions. Their appearance in color and consistency varied, however. The metallic soaps such as copper and iron from Ivory had the color characteristic of the metal but much lighter than the same metallic soap from cottonseed oil. The soaps from Ivory were much more dry and powdery than those from either Castile or Cöttonseed oil soaps. The Castile however resembled those metallic soaps made fsom pure oleic acid while, the Ivory resembled those from pure stearic acid so the commercial soaps were used instead of the pure soaps. The ferric, nickel,cobalt and strontium werefrom castile were not dry nor powdery but amorphous and soft.

Along with the metallic soaps discused above might be mentioned aluminum soap. The soap being so much more important than the others, since it was the principle soap studied in the experimental work a separate section is given to it. Its peculiar properties gives it an important place among the metallic soaps. It seemed to posses properties different from the rest of the metallic soaps and these seem to place it in a class by itself.

Aluminum soaps were prepared from the samples of pure soap made previous to this and their separate properties will be taken up.

Pure potassium stearate soap was put into solution in distilled water heated and a solution of alum was added to it. A precipitate of aluminum soap was at once formed which did not adhere but was rather a fine white precipitate. To remove it from the solution it was filtered by a suction filter. When dried it appeared as a white dry granular mass.

Pure potassium oleate solution to which an alum solution had been added gave an aluminum soap which was exceedingly sticky. It did not come down as a granular precipitate like the stearate but lumped together and formed on the top and could easily be skimmed off.

Aluminum soap from potassium linoleate was dark in color, not so sticky as the oleate and resembled that of aluminum stearate, being granular and rather dry.

Aluminum palmitate was formed on the top of the solution when alum solution was added to potassium palmitate. It gathered in lumps and could be removed with the fingers or by a stirring rod. It was a sticky, dough like mass.

Cottonseed oil soap solution have an aluminum soap which was similar to that prepared from pure potassium oleate. It was a thin sticky soap. As the cottonseed oil soap was a cheap soap and since in appearance and consistency its aluminum soap is the same as that from pure oleic acid it was used in place of the latter.

A small amount of ammonium hydroxide soap from palmitic acidwas dissolved in distilled water and to the solution, aluminum solution was added, there was a flaky white precipitate of aluminum soap. It was neccessary to filter this to obtain the soap and when dried it was a white powdery substance.

In a solution of the lithium soap, aluminum soap was precipitated. It was a doughy yellowish mass which adhered to the stirring rod and very much resembled the aluminum soap precipitate from Ivory soap.

These above aluminum soaps were prepared merely for reference and to see which commerical soap would serve the same purpose. It was found that the Ivory soap gave an aluminum soap which was far ahead of that from the pure soaps as it was formed on the top of the solution in a tough doughy mass and could be handled with the least trouble. Filtering was not necessary as a great deal of the water could be removed from the soap by squeezing. When moist it resembled thick bread dough and was as elastic. When dried in the air for any length of time or even in an oven it become more powdery but still retained its gummy feeling. In the experiments that followed when aluminum soap was needed the soap from Ivory solution was used. The reason that Ivory soap has the properties that it does, (that it forms a metallic soap not too liquid like cottonseed oil and one not too dry like the Kirk's Flake White soap) is because the oil used for making the Ivory soap is cottonseed oil which has been hydrogenated. Cottonseed oil is an unsaturated oil and therefore one of the softer of liquid oils but it may be hardened or made somewhat harder by hydrogenation, because it is so hardened makes it the ideal oil for soap.

The aluminum soap from Kirk's Flake soap was granular and in appearance resembled ground meal. It was almost identical with the aluminum soap from pure stearic acid which showed that stearic acid was the principle acid in Kirk's Flake White soap. It was necessary to filter off the soap and because of this it was discarded in the experimental work.

Castile soap made from pure olive oil gave an aluminum soap which was gummy and rather sticky. The high cost of the castile soap at once made it impracticable for experimental use and for commercial use as well.

SOLUBILITY OF SOAPS

After preparing the metallic soaps it was then necessary to find a solvent for them. Not all of the metallic soaps were tried only those which seemed to be the most promising for commercial use or experimental work.

The following metallic soaps precipitated from cottonseed oil soap solution were determined.

Calcium was practically insoluble in gasoline, and alcohol. Barium was just slightly soluble in gasoline and ether. Cobalt seemed to go into solution in gasoline when solvent was hot but on standing it settled out. The ferric soap could be dissolved only slightly if at all in gasoline, ether, and alcohol. Chromium was very soluble in gasoline when gasoline was hot that is the soapsseemed to be alliin solution but when the solution was cold a relatively large amount of chromium soap settled to the bottom of flask indicating its insolubility in cold gasoline. Nickel soap went readily into solution in gasoline and even when it stood weveral days it did not settle out. Magnesium was quite soluble in gasoline just a very small amount settled out on standing . Ferric was soluble in gasolin if the soap was not allowed to dry but if the moisture was absent only a very small amount if any went into solution. It was insoluble in ether and alcohol. Ferrous soap was much less soluble than the ferric and did not go into solution even when heated. The lead seemed very soluble in gasoline when being heated as the solution was very clear but when the flack was cooled down the soap came down as a heavy precipitate. The zinc soap was slightly soluble in gasoline. Copper was readily soluble in gasoline that is when soap had moisture present.

The same soaps as above were precipitated from Ivory soap solution and their solubilities tried in gasoline. Nickel was not so soluble as that from cottonseed oil but was not entirely insoluble. The copper was very soluble in gasoline. Zinc was very soluble when gasoline was hot then solution was clear but when cooled a large amount of soap was precipitated. The lead soap like that from cottonseed oil was insoluble in cold but readily went into solution when heated. Chromium was only slightly soluble. Calcium was readily soluble. Ferric soluble but ferrous not.

The same metallic soap were not soluble in alcohol nor ether, that is readily soluble, asonly a small amount went into solution after being heated for several hours copper soap from Ivory seemed to be an exception and went into solution in ether in the cold.

The main point concerning the solublities of the soaps is that they are not soluble when all water is absent.

Aluminum soap readily went into solution in gasoline making a smooth homogenous solution resembling water-glass solution. Chloroform also dissolved it and made a clear smooth solution very much similar to the of gasoline. It was as readily soluble in chloroform as it was in gasoline and on standing several months no sediment was noticeable in the bottom of the flask. Ether, alcohol and chlorine failed to dissolve the soap.

One very striking fact was observed and that was that when the aluminum soap had been air dried it did not go into solution so readily and often no appreciable amount went in. When this was discovered the soap after being air dried was dried in an electric oven for a day and a half. Then the gasoline which was to be used as the solvent was freed from all water by distilling over calcium oxide. The two were then mixed the gasoline free from water and soap free from all moistrue, and refluxed for several hours. When the solution had settled 100c. of the clear liquid was removed and placed in a watch glass and the gasoline evaporated off, the residue left on the dish indicated the amount which had gone into solution and the amount was so small that only a very thin cooling of it was deposited upon the dish.. This indicated the some moisture was necess ary for the soap to dissolve. This shows that the soap solutions are really colloidal emulsion and possesses the striking characteristics of colloids.

COLLOIDS

Soap is one of the many substances which comes under that peculiar class of substances known as colloids and about which so little is known and much is surmised. Colloids are more widely distributed in nature than are crystalloids and yet more is known concerning crystlloids while colloids have been only scientifically studied for fifty years.

Graham who did a great deal of work on colloids considered them and crystalloids as "two distinct worlds of matter". He drew this conclusion because the crystalloids were capable of passin g thru a simipermeable membrane and the colloids showed inability to diffuse thru such a parchment. Hundreds of substances have been obtained as colloids and these comprise elements as well as practically all types of chemical compounds; and it has been recently emphasized that the possibility of converting a substance into a colloidal substance has no relation what-so-ever to the chemical character of ther substance. Von Weimarn asserts that any substance may be obtained in the colloidal state provided the correct conditions prevail. Properly speaking we should then speak of a substance as in a colloidal state and not as a colloidal substance. As there are different degrees of solubility so there is a marked difference in the ease with which various substances assume the colloidal state, for it is a state or condition of matter, the same as gas, liquid and solid are states of matter. The study of the colloidal state comprises "colloid chemistry", which is an important division of physical chemistry and is assuming as prominent a place as electro-chemistry, thermo-chemistry, and radio-chemistry.

We may define colloid chemistry as chemistry which deals with the behavior and properties of matter in the colloidal condition, which as we now know, means a certain very fine state of subdivision. While there are no sharp limitations to the size particles in colloidal solutions, it may in a general way be stated that their sphere begins with dimensions somewhat smaller than a wave length of light and extends downward well into dimensions which theory ascribes to the molecules of crystalloid.

A number of substances are known to exist both as a crystalloid and as a colloid. Sodium chloride which is usually known as crystalloid, can be obtained in the colloid form while albumin which is usually classed as a colloid, may be crystallized.

Colloidal state, then is of the nature of a heterogeneous system, or a system of more than one separated phase. The point of importance to be remembered is that the phases of which the system consists are separated from one another by surfaces, interfaces, of contact. The colloidal state differs from a coarsely heterogeneous system, such as a mass of gold immersed in water, in that it is to ordinary observation, homogeneous, and only shows its micro-heterogeneous character by special methods of investigation. On the other hand, it is distinguished from true solutions of small molecules or ions by the fact of the possession of surfaces of contact, with all the phenomena implied by this. These properties will naturally by especially marked on account of the great surface area due to the minute state of subdivision.

It is convenient to have names for the two phases of which a colloidal system usually consists. Hardy gave them the names of "internal" and "external" phases, other investigators called the "internal" the "dispersed phase" or it corresponds to the solute; the "external phase" is called the "continuous" or "dispersing medium" and is similar to the solvent.

The two phases of which a colloidal solution consists may obviously be of many various kinds.

1 Liquid as the disperse means; when the disperse phase is a

(a) Solid, they are termed suspensions
(b) Liquid, they are termed emulsions.
(c) Gas, they are termed foams.

2. Gas as the disperse means; we have when the disperse phase is a

(a) Solid-smoke (tobacco smoke); condensing vapors of metals (ammonium chloride, cosmic dust.
(b) Liquid, atmospheric fog, clouds, condensations of steam.
(c) Gas, no example known

3. Solids as the disperse means; we have when the disperse phase is a

(a) Solid, known as solid solutions, mixed cyystals, carbon particles in iron and ruby glass.

(b) Liquid, occension of water, emulsions or emulsoidsas milk

(c) Gas, solutions of gases in solids, gaseous inclusions in minerals.

This classification is then in harmony with Baucraft's definition "colloid chemistry is the chemistry of bubbles drops filaments and films."(1)

The system is in many ways a useful one, although it does not direct attention to what is perhaps the most important distinction between different classes, that is the affinity of the dispersed phase for water. When the internal phase, although a liquid, is in extremely minute droplets, its mechanical properties closely resemble those of a solid, the great pressure due to the internal component of the surface tension confers rigidity on them. The characteristics in the general behavior of a colloidal system ~~is the~~ affinity of the internal phase for water. The more water the internal phase contains, and it may contain as much as 90 percent, the less will be the difference between the properties of the two components of the interface of contact between it and the external phase and consequently the less will be the surfact energy.

Zsigmondy divided colloids into two classes, the reversible and irreversible; the former redissolve after dessication at ordinary temperatures where as the latter do not.

With the reversible colloids (gelatin, gun, arabic, albumin), there is a more intimate reunion between the two phases; in fact it is probable that with them we have really a mixture of (1) a dispersed phase of water subdivided in the solid with (2) a dispersing phase of the solid finally subdivided in water. The former are there-

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(1) Lincoln's Physical Chem. pg.443

fpre called emulsoids and the latter suspensoids, or emulsions and susperisions. By suspensions we mean the floating of a powder in a fluid such as clay in water. An emulsion is the minute division of one fluid in another with which it does not mix,,for example, oil in milk or water. The smaller the particles of the"dispersed phase", the longer it takes for them to separate. Such a suspension or emulsion in which the dispersed phase is easily distinguished microscopically may last for monthe and even years. Many discussions have arisen whether colloidal gold, silver and arsenic sulphide were suspensions or true homogenous solutions. They cannot be separated from their solvents by mechanical means (filtering and centrifugation) A substance is said to be homogeneous if all its mechanically separable pariticles posses the same composition and physical properties. There is no difinite solubility in respect to suspensions and emulsions, for within certain limits we are able to suspend as much clay or emulsify as much fat as we wish, the "finer" the clay or the fat is subdivided, the more dissolves, and the same thing holds true for colloids.

We can obtain supersaturated solutions of crystalloids and certain small additions increase the solubility disproportionatily. Such additions when employed in the case of colloids and suspensions are called "protective colloids" because they protect the clay or finely dispersed silver from separating out.

The difference was thought to be that colloids did not crystallize out. A few, however do as egg albumin, and hemoglobin. Colloids usually separate from their solution in unformed masses called gels. Some gels separate free from water, others do not; nearly all natural organic solutions do not. The amounts of water held in the gels has wide limits of variation. Colloids which precipitate a practically free hydrogel are called hydrphobe and those which produce hydrogel swollen and rich in water hydrophile colloids.

Or colloids which when precipitated by addition of electrolytes and cannot be brought back again into the finely divided state are said to be lyaphobe. The precipitating action of well ionized electrolytes is doubtless connected with the fact that the metallic particles in the suspensoid solution are electrically charged with regard to the solvent. That they are so charged may be proved by immersing two electrodes in the solution, when it is found that the particles travel to the anods, indicating that they carry negative charge; most good electrolytes effect the precipitation, and the concentrations required are usually small. In the case of particles carrying a negative charge, the precipitation appears to be effected chiefly by the positive ion, and take place the more readily as the valency of the positive ion is greater.

In pure water nearly all suspensoids are charged negatively, the chief exceptions are the metallic hydroxides, which have a positive charge. When two suspensoid solutions of apposite electrical charges are mixed the particles at once precipitate each other.

A typical emulsoid solution (gelatine or agar-agar) shows heterogeneity under the microscope, but is very different in its properties from a suspensoid solution. The suspensoid solution is mobile, while the emulsoid is viscous even at small concentrations, and at greater concentration sets to a stiff jelly on cooling. The emulsoid solution, again, is not coagulated by the addition of small quantities of electrolytes. The addition of large quantites of neutral salts, however, may effect the coagulation, but in this case the reaction is reversible, that is, the coagulum can again be brought into emulsoid solution in pure water, colloids of this type are said to be lyophile.

GENERAL PROPERTIES OF COLLOIDAL SOLUTIONS

As has been mentioned before in the whole theory of colloidal solutions we are assuming that we are dealing with two phase systems. The two phase theory however is disputed by some people but there are certain properties of colloidal solutions which prove the two phase theory. If a beam of light strikes small particles in suspension in a transparent medium, the light is scathered and polarized, provided the refracture index of the particles differs from that of the transparent medium. The scattered light is therefore chiefly blue. This is known as the Tyndall phenominon and it was used by him to determine whether air was free from dust and was optically empty. The same principle has been perfected and applied in the ultra-microscope. In this instrument a powerful beam of light is focussed on the liquid to be examined and is looked at from the side by a powerful microscope. If there are suspended particles in the liquid they appear as bright spots. One does not see the particles themselves but merely the light diffracted by them. With colloidal gold in glass it is possible to see that we have a two phase system. By means of some form of this instrument it is possible to demonstrate the existence of a second phase in many colloidal solutions.

The presence of a second phase in a colloidal solution can also be shown by what is called ultra-filtration. A colloidal solution goes right thru an ordinary filter but Bechhold showed that it was possible to form on filter paper or wire gauze, collection films with varying amounts of acetic acid or gelatine films hardened with formaldehyde, such that pores of almost any desired size can be obtained. By taking a filter with sufficiently fine pores, almost any colloidal solution can be filtered so as to leave the suspended matter behind. With a more porous filter the finer particles go thru and the coarser ones are held back. In this way it is possible to get an approximate idea of the relative size of the particles in two different colloidal solutions. Blue colloidal solutions of litmus have finer particles in them than the corresponding red solutions.

Since the existence of a colloidal solution depends upon the Brownian movements counteracting the force of gravity, it follows that if we increase the force of gravity, a colloidal solution will become less stable and may precipitate. This can be obtained by centrifuging. Some colloidal solutions may thus be precipitated and a good example is the separating of cream from milk. The converse is also true that a solution becomes more stable against centrifuging if the particles are made smaller.

A coarse suspension, if entirely insoluble and anhydrous, should give rise to no osmotic pressure, no diffusion except as a result of electrical charges, and no change in surface tension or conductivity. If the suspension is hydrous it may have a marked effect on the surface tension. In general the apparent osmotic pressures of colloidal solutions are very small and this has led to absurd molecular weights.

The low rate of diffusion of colloids was the phenomenon which first started Graham on his studies in regard to colloids. There is no question but that colloids do diffuse. This may be due in part to adsorbed material, but we also get a diffusion due to the Brownian movements. The diffusion of a colloid through certain membranes is practically zero, while true solutions go through readily. This is made use of in separating colloidal materials from dissolved substances. This process is called dialysis. The dissolved substances diffuse out and the colloidal material is left behind.

The viscosity of a liquid is the resistance offered to shearing, to stirring or to the flow thru a capillary tube. In the case of water soluble colloids the viscosity may increase enormously with the concentration, a one percent solution of agar forming a solid jelly. This is undoubtedly in part a question of structure just as we know it is when 99 percent of kersene is emulsified in a one percent of asoap solution. Here we have minute globules of oil coated by viscous soap films which coalesce to form a honey comb structure. The metal and the sulphide solutions have only a very slight effect on the viscosity of water. This varies with the nature and the sub-division of the solid particles. The viscosity of colloidal soap solutions has been found to vary. (containing different electrolyie solids).

The particles of practically all colloidal solutions possess an electric charge and under the influence 6f an electric current difference of potential move toward the electrode having the opposite charge. The rate of migration of colloidal particles is of the same order as that of ions. Thus colloidal silver moves with a velocity of 2.0-3.8 per seconed under a potential drop of one volt per-centimeter, and colloidal gold at about 4.0 per second, while the chlorine ion gives a value of 6.8 per second.

The electrical transfer of particles through the liquid is called cata phoresis and the transfer of liquid thrua stationery diaphrogn is called electrical endosmose. It was first abserved by Reuss at Moscow in 1808. Working with so-called pure water it is found that water posses to the cathode when the porous diaphragmeis made of glass, shellac, earthenware, carborundum, asbestos, platinum ,silver, arsenic sulphide of sulphur; and to the anode when the diaphragm is chromic chloride, cabolt oxide, zinc oxide or barium carbonate. When turpentine was substituted for the water it would to the anode with all diaphragms except sulfur. Coehn has attempted to account for this emperically by saying that when two nonmiscible substances are in contact, one being a pure liquid, the substance with the higher dielectric constant is charged positively with reference to the one with the lower,dielectric constant. This is known as Coehn's Law and depends upon the relative adsorption of ions and is useful in certain cases but does not hold good for allsolutions.

In the investigations of Powis he showed that a colloid could be made to have either a positive oraa negative charge depending upon its preparation and he prepared colloidal solutions of ferric hydroxide with a positive charge and solutions with a negative charge.

It has been known for some time that on addition of a very small quantity of certain electrolytes to suspensions, emulsions or colloids the corresponding substances are thrown out of solution and form flocculent precipitates (gels) or in the case of emulsions, the oil collects as a layer on the surface. A certain minimum quantity of electrolyte is necessary to effect this. This is far too small to small to make the process analogous to the salting out process where large quantities of the salt are required. The precipitating of the metallic soaps from the soap solutions would be classed as salting out.. Hardy, Schulze Law states that "the important generalization is that ions carrying a charge of sign opposite to that carried by the colloid are the most active precipitants and at the same time the higher the valency of the ion the greater its precipitating action". This coagulating may also be brought about by heating, or cooling the colloidal solution as well as by electrolytes, the particles being carried in virtue of their charge to one of the electrodes where they become discharged and assume the gel form. Favorable conditions for bringing about coagulation of colloids is the adsorption of an appositively charged ion. If one colloid can adsorb another, then if the charges are opposite in sign, it is to be expected the coagulation or precipitation of both will take place. The amount necessary to precipitate the colloid will vary with the degree of adsorption; it will be a specidic property and not an additional one. Solutions having the same charge are not precipitated.

Reversible coagulations is met with in the case of gelatin when the coagulation has been brought about by temperature changes. This reversibility is spoken of as peptization. The word was coined by Thomas Graham, the father of colloid chemistry to express the liquifaction of a gel because he noticed that there was a great resemblance between digestion and colloidal disintegration. Peptization is the disintegration of particles so that they may form a colloidal solution. Certain solutions will peptize or disintegrate certain precipitates so that we get colloidal solutions. This is always the result of adsorption. Theoretically there are three possibilities. If an adsorbed film has a low surface tension on the water side and a high one on the other side, it will tend to scrunch up and to peptize the solid as internal phase. If the reverse is the case, the solid will tend to form the external phase. If the two surface tensions are practically equal neither will prevail. Some adsorbed substances seem to have practically no peptizing action. We may have peptization by a liquid, by a non-electrolyte, by an adsorbed ion, by a salt or by a peptized colloid. When a liquid is adsorbed by a solid it will tend to peptize it and in some cases will do so. Water peptizes tannin, amyl acetate peptizes pyroxylin and fused baths peptize metals. At higher temperatures the peptizing action increases,and we may get glass peptized by water or vulcanized rubber by various organic liquids.

There are a number of cases where mixed solvents will peptize a solid much better than either one above--cellulose nitrates in ether a and alcohol, caseine in pyridine and water and probably cinchonine in choloform and alcohol,as well as phlaretine in ether and water.

Relatively little work has been done on direct peptisation by means of a dissolved non-electrolyte but a number of cases are known where a non-electrolyte prevents the formation of a visible precipitate. A concentrated solution of sugar in water will prevent the prepipitation of calcium silicate, silver chromate, and silver chloride.

If one ion of an electrolyte is adsorbed more than the other ion, it will tend to peptize the adsorbing material and to give rise to a colloidal solution containing positively or negatively charged particles according to the nature of the adsorbed ion.

The inability of the aluminum soap to go into solution or rather to form a colloidal solution in the absence of water is directly related to the theory of peptization. In this case water was necessary to disintegrate the particles of the aluminum soap so they would form a colloidal solution. Water was the peptizating agent and without water to peptize the soap refused to form a colloidal solution in the gasoline. Aluminum soap was not the only metallic soap which needed water to peptize it but the other metallic soap needed water also. Since metallic soaps form colloidal solutions they seem to have this one outstanding characteristic of some colloidal substances that they will not go into solution again or rather form a colloidal solution unless water is present to peptize it.

SOAP AS AN EMULSIFYING AGENT.

In the discussion of colloids we have mentioned emulsions which consists of drops of one liquid suspended in another liquid and as soaps are so closely related to colloids and especially emulsions it seems fitting in this connection to take up soap as an emulsifying agent.

An emulsifying agent is a substance which goes into the interface and produces a film having satisfactory physical properties. The necessary conditions for forming a stable emulsion are that the drops shall be so small that they will stay suspended and that there shall be a sufficiently viscous film round each drop to keep the drops from coalescing. The sinplest way to emulsify oil in water is to add a water soluble colloid which is adsorbed strongly at the interface and the simplest way to emulsify water in oil is to add an oil soluble colloid which is adsorbed strongly in the interface. As a matter of fact this is the way in which almost all emulsions are made. Sodium and potassium oleates are water-soluble colloids and they are excellent for emulsifying oils in water. The gums are also water soluble colloids. Gelatine is a water-soluble colloid but it is not used much as an emulsifying agent probably because there is too much danger of putrefaction. By adding salt to a soap solution; the soap film can be made to come out so brittle that it will not form a satisfactory emulsion.

Pickening (1) made emulsions of kerosene in water with small amounts of soap as the emulsifying agent. With 70 to 80 percent of kerosene the mass was viscous and with 99 percent oil it was as stiff as blanc-mange, and could be cut into cubes which would stand alone.

Calcium and magnesium oleates form colloidal solutions in oil and can therefore be used, its emulsify water in oil. If water is stirred into a heavy lubricating oil containing a lime soap, the water will be emulsified in the oil and will change it to a grease, instead of decreasing the viscosity as might perhaps have been expected.

The water in butter may be emulsified by means of a calcium soap; but more probably the water is merely dispersed as drops in a viscous medium without any true emulsion being formed.

In making emulsions of oil in water by means of sodium oleate it must be remembered that the soap does not go entirely into the interface. There is always a relation between the concentration of the soap in the interface and the amount still peptized in the water. It is a care of the distribution of soap between the water and the interface. Any thing that cuts down the peptizing action of the water an the soap will increase the amount going into the interface and anything increasing the peptizing action of the water will decrease the amount of soap in the interface.

Since sodium oleate emulsifies oil in water and calcium oleate emulsifies water in oil, a mixture of the two oleates will behave differently, depending on the relative amounts. There is same ratio of calcium to sodium at which the two oleates will practically balance each other and the slightest change in this ratio changes the type of emulsion. It has been found that this ratio necessary to produce a balancing, between these two types of emulsion, when working with water, oil, and soap is practically the same as that found in Sea water.

ALUMINUM SOAP AS A PRESERVATIVE

Since aluminum soap is such an excellent preservative for eggs, it was decided to try the soap on fruits and vegetables. Apples were first tried; one apple was dipped first into boiling water and then into the aluminum soap solution; the other apple was dipped into the gasoline soap solution at once. These were then left in the laboratory for several weeks and examined occasionally. The apples used were apples that had no bruised or bad spots on them but at the end of two or three weeks the apples showed signs of spoiling and a week or two later the apples were brown and soft. The apples although having been dipped into the gasoline soap solution did not taste of the gasoline. Both apples, the one dipped in hot water and then in gasoline and the one dipped directly into the solution, spoiled in the same length of time. Other apples were tried in the same solution but none of them kept for any longer period than the first ones. Some of the apples were dipped into the chloroform solution of the soap but they likewise were spoiled at the end of several weeks. Although the apples were preserved for a longer period than they would have had they not been dipped into the solutions.

Oranges were also dipped into the solution and as above some were first dipped into hot water and others into the gasoline solution without first being dipped into the hot water. There was no difference observed in the results as the oranges although at the end of fime or six weeks were not spoiled yet, the peeling became dry and shrivelled and to all appearances were spoiled. The oranges ~~dese~~ were cut open and eaten they were not spoiled inside neither did they taste of the gasoling. The peel became dry and as tough almost as leather altho the orange itselfwas not spoiled.

Sweet potatoes were treated in the same way as above and those kept for several months. They were dipped into the soap solution on February 15 and are still good, yet somewhat shrivelled. They were cut open examined and tasted. They seemod firm on the inside and did not taste of the gasolino.

However, there is a great possibility that the soap could be used as a preservative for fruits and vegetables and its favorable property is that it does not impart the odor of gasoline to the fruit and vegetables. The gasoline seems to evaporate and not penetrate the skin of the fruit.

WATERPROOFING

The solution for waterproofing cloth and leather was prepared by dissolving a large amount of aluminum soap, which had been precipitated from Ivory soap solution, in gasoline, The cloth to be waterproofed, kahki in the case, was soaked in the gasoline soap solution for a week.

At the end of this time it was removed and dried in the air. The appearance of the cloth was exactly the same as before.putting into the solution. The is one point in favor of the solution that no harm is done to the material being water proofed. The cloth was placed over a large dish and water poured upon, and some water left upon the cloth for several hours and no water had soaked thru the cloth. A very severe test was also made upon the cloth by rubbing the water into with the fingers and after this treatment some water only a very small amount, did pass thru, but just enough to moisten the cloth on the other side. Several samples were thus treated and result s were always the same. A laboratory apron made of this same material was immersed in the solution and left for a week then dried and treated in the same manner as the samples.

A small sample was placed in the gasoline solution and flask connected with the vacium, by this method the air was drawn out from pores of cloth and when vacium was removed the solution filled the pores of the cloth but the results were not any great improvement upon the previous method of leaving the cloth in solution.

A large piece of cast iron was cleaned and half of the metal dipped into gasoline soap solution. The cast iron was then placed upon the roof of the chemistry building and left exposed to the weather for three months or more. When examined the part which had been dipped into the solution had not rusted at all, while the part which had not been in the solution was covered with thick layer of rust. This soap solution proves to be an excellent solution for metals to render them weather proof and therefore ought to be of practical use.

Leather to be waterpfoofed was treated in the same manner as the cloth and metal. The leather was just as resistant to the water as the other materials had been.

A solution of aluminum soap in chloroform was also tried although it was as successful, yet the gasoline solution seemed to be the more ideal solution to use.

DIALYZERS

Porcelain cups which might be used as dialyzers were put into a suction filter in the aluminum soap solution. The vacuum was then turned on and the air drawn out of the pores of the cup. When the vacuum was removed, ~~and~~ the solution entered the pores. The cups were then dried in the air, filled with a concentrated sugar solution and two of the cups placed in the thermostatic bath which was kept at constant. temperature and two in a dish of water at room temperature. In a day or two the water in the dish became sweet indicating that the solution had passed thru the cup into the dish.

The same treatment as that above was given two porous cups dipped in chloroform solution andthe results were identical with those above and this solution could be used in place of the gasoline.

MORDANTS IN DYEING

Some of the metallic soaps, whose compounds are often used as mordants in dyeing, (nickel, magnesium, aluminum, chromium and copper) and which had gone into solution in gasoline were tested, to determine whether or not the metallic as well as its other compounds would not serve the purpose of a mordant.

A small sample of cotton cloth was washed well with soap and hot water, rinsed, and dried and placed in a solution of malchite green. This sample was merely for a standard or a check with which the other samples were to be compared. When dyed it was a very pale green. A second sample was placed in a solution of magnesium soap heated and then put into the malachite green. The cloth when dried was just as light in color as the one not mordanted. When a sample was dipped into the concentrated solution and heated for about ten minutes or longer and then put into the dye the cloth came out a very dark green much darker than the sample not mordanted but when dry and washed thoroughly with strong soap solution it became lighter, yet still a few shades darker than the non-mordanted one. The soap which gave the darker colors were nickel and chromium, but they became lighter like the copper soap when washed with strong soap solution especially the chromium.

LUBRICANTS

The waste product from the refineries called "B.S." was treated with various metallic soaps.

To one sample of the "B.S." was added aluminum soap which went into solution much more rapidly then it did in gasoline.

About ten or fifteen grams of the aluminum soap could be dissolved in 20cc. or less of the "B.S." this gives some idea of its solubility in this waste product. As the soap was gradually added the resulting mixture became less and less viscous, first the consistency of a lubricant then past that stage into a more elastic and rubbery compound. The sample was merely an experiment to determine the amount of soap which could be dissolved in the "B.S."

To a nother sample of "B.S." was added a solution of cottonseed oil soap and the mixture heated, the water present in the soap separated out from the rest of the solution and could be poured off. The resulting solution was a smooth thick substance not so thick as axle grease but as smooth. To a third 20cc. was added Ivory soap which had been ground up fine, and heated. The soap did not readily go into solution and when cooled was lumpy or grainy. An alum solution was added to 20cc. of "B.S." and to an equal amount a solution of Ivory soap. These two mixtures were then put together with the idea that the alum might precipitate the aluminum soap in the "B.S." and give the consistency desired for the lubricant, but the result was that instead of a smooth, more solid compound, it was grainy and soft. It was then decided to try a calcium or barium soap with "B.S." Both soaps went readily in solution in "B.S." and gave a consistency to it closely resembling that of lubricants. The barium soap however seemed smoother than did the calcium and so it was decided to use the barium in place of the calcium. The best results however were obtained by mixing aluminum and barium soaps; a substance with appearance and consistency of lubricants was then obtained. It is evident that a lubricant made from "B.S." would mean a great deal for Oklahoma as then there would be no waste products at the oil refineries but the substance which they now discard would be converted into lubricants at very little cost.

FILLERS FOR WOODS

Aluminum soap solution was applied to a new board to determine whether or not it might be used as a filler.for wood. To one part of the board aluminum soap was applied; to anothe r part ~~part~~ shellac and to a third section a mixture of aluminum soap and shellac. When the board was completely dried varnish was put on and when dry examined, there was no difference in the appearance of the shellac and the aluminum soap as fillers. ~~and~~ Therefore the soap will serve the same purpose and is a great deal cheaper.

SUMMARY

In our experimental work many interesting, useful and important facts from a practical standpoint have been obtained.

1. That there are great possibilities that aluminum soap dissolved in gasoline being used as a preservative for fruits and vegetables as no taste of gasoline was imparted to the fruits.

2. Aluminum soap dissolved either in gasoline or chlorlform imparts to porous cups the properties of a colloidal membrane.

3. Nickel, chromium, and copper soaps serve the purpose of mordants in dying cotton. The copper soap being the best.

4. A mixture of aluminum and barium soaps in "B.S."(the waste product from the refineries produces an exle grease and suggests a method of utilizing this product.

5. It also makes an excellent wood filler and maybe used as substitute for shellac

6. Gasoline solution of aluminum soap is an excellent waterproofing material and rendered cloth, leather and metals impervious to water when they are dipped into it, an exellent material for tents and coverings for heavy shoes and for machinery which, has to be left out in the weather unprotected. Its is an improvement over the old method of passin cloth to be waterproofed thru a soap solution and then thru alum solution to precipitate the aluminum soap in the cloth. It is also evident that a waterproof aluminum paint might be made from this solution also for waterproofing and painting metals.

7. There was were found new soluvents heretofore not mentioned in the literature, chloroform and ether for aluminum soap, gasolin for nearly all the metallic soaps.

8. In order to obtain a solution of the metallic soaps the soap must be wet. No solution obtained if soaps are entirely free from moisture.

9. Soaps made from unsaturated oils are most readily soluble. Metallic soaps from cottonseed oil soap were readily soluble; those from Ivory soap (which is prepared from hydrogenated cottonseed oil) are next soluble; the soaps from stearic acids the least soluble.

10. It was also evident that the soaps made from the oils having the smallest molecular weights were more soluble than those of higher molecular weights.

Aluminum soap solution was applied to a new

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