ALKALIES IN THE WASH WHEEL

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WHILE soap is the primary detergent material used in power laundry washing procedures, the need for an alkaline agent as a supplement to soap has long been recognized. Alkaline materials commonly applied include caustic soda, sodium metasilicate, trisodium phosphate, soda ash, modified soda (sesquicarbonate), and mixtures of these materials.

That the choice of alkaline materials as well as the quantities to be used with soap has not been well defined is clearly evident from the widely varying methods used in practice. For somewhat similar operating conditions for white cotton fabrics it has been observed that this variation is so great that in one instance a laundry may be using the weakest alkali, modified soda, in a proportion of one part to two parts of neutral soap to provide pH values of less than 9.5 in the sudsing operations while for apparently identical purposes another laundry may apply caustic soda in quantities sufficient to provide alkalinities of pH 11.5 or greater. From this observation there may be drawn the conclusion that either the mechanism of detergent action is not specific in respect to alkalinity as expressed in pH or that one, or even both, of the operators are wrong. While critical observation of the work produced will invariably indicate that a condition of higher alkalinities is distinctly superior there still persists a wide difference of opinion on the optimum pH for maximum efficiency. A large part of this divergence of opinion is undoubtedly based upon a lack of understanding of the process, while another portion is unfortunately based upon the desire to apply products no longer suited to modern operating conditions.

A clear understanding of the soil in clothes would immediately suggest to some degree the course of study to follow, but unfortunately this widely varying and truly unknown quantity has yet to be defined beyond an empirical listing of the common substances that obviously may be deposited upon fabrics during their normal service or use.

Washing Procedures

To remove this unknown quantity called dirt, the modern laundry applies a formula involving a series of alkaline sudsing operations that are intended to remove all soluble and insoluble foreign substances from the fabric. If the textile dyer has applied a dyestuff that is more loosely attached than the soil, the colored fabric may fade, which is no fault of the laundry. Since a number of the foreign substances attach themselves to fabrics as insoluble stains not removable by sudsing operations, the next procedure is to apply a bleaching agent, sodium hypochlorite or hydrogen peroxide, with the hope that by oxidation the stains will be rendered soluble or colorless or preferably both. The use of a bleach in moderate quantities is well justified by the results as the general whiteness is improved, a few types of stains are definitely removed, and the strength of the fabric is but little affected. The stains that are inert to oxidizing effects remain and any misguided efforts to remove these stains by greatly increasing the quantities of bleach are of no avail but do have the unfortunate effect of reducing the strength of the fabric and hence shortening the life of the garment. Colored fabrics bleached with hypochlorite are frequently adversely affected hence only peroxide should be used on colors if bleaching is necessary, as this material does not affect dyestuffs.

After sudsing and bleaching, the fabrics are rinsed by successive changes of water to thoroughly remove all substances previously dissolved or suspended as well as the supplies that have been added. Any iron rust stains or certain types of ink stains can then be made soluble and removed by a hot treatment with small quantities of the acid fluoride salts. Adequate rinsing after this souring treatment leaves the clothes slightly on the acid side so that starched work will not yellow from the effects of small quantities of bicarbonate alkalinity found in most water supplies.

The clothes are now sterile, white as when new, and retain only the stains that are insoluble and chemically inert to mild alkalies, mild acids, and oxidizing agents. A few stains that respond to reducing agents may be treated by hand. The remaining stains (or soil) consist of a wide variety of medicinal preparations, carbon particles that have become too well attached, paint pigments, metallic oxides and the innumerable but seldom identifiable substances that people somehow come in contact with accidentally. Many of these substances are as firmly affixed as a good dyestuff or the fibers themselves while others might respond to a more thorough or intelligent treatment. The fabric is intact with less than a loss of one-half of one per cent in strength if properly handled, which in turn is considerable less than the wear it received getting dirty.

Review of Process

In reviewing this process to determine how a better job could be done with even less effect on the fabric there are listed, in order of decreasing effect on the fabric, the several factors involved:

1. Bleach: Misused, this is by far the most destructive factor. In moderate quantities it may run second.
2. Mechanical action: An increased number of sudsing operations increases the effectiveness of the formula but likewise increases mechanical wear that is most noticeable on edges of collars, seams, and turned selvages. A reduction of time or operations would be advantageous.
3. Soap: In its lubricating effect soap allows fibers to slip and loosen in the twisted yarns. By its detergent action it removes poorly affixed dystuffs in the same manner as it removes soil. However, the benefits greatly exceed any detrimental effects.
4. Sours: If oxalic acid is used in excess, it would be damaging to cotton fabrics. Otherwise sours would be placed last.
5. Alkalies: By nature, cotton

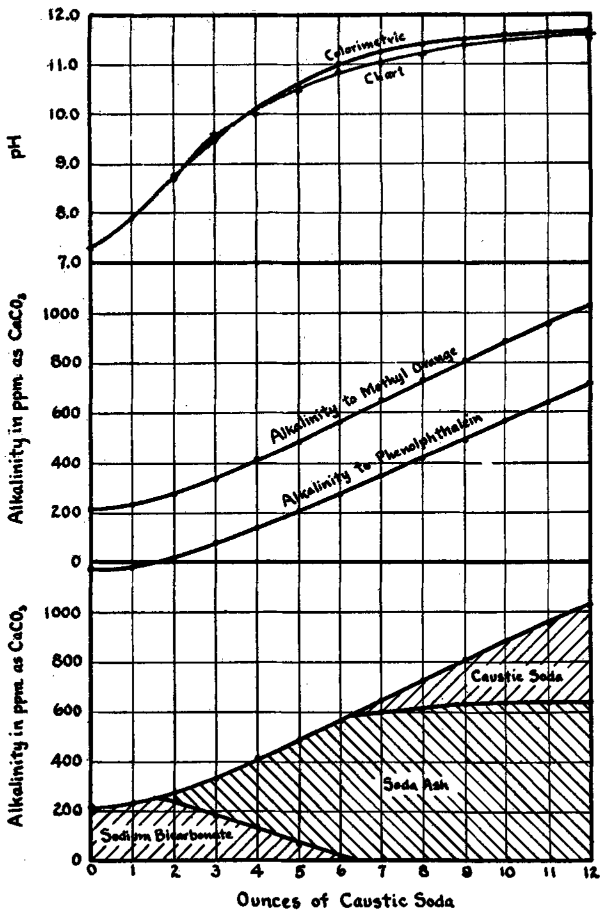

Chart I. Caustic Soda on Family Work

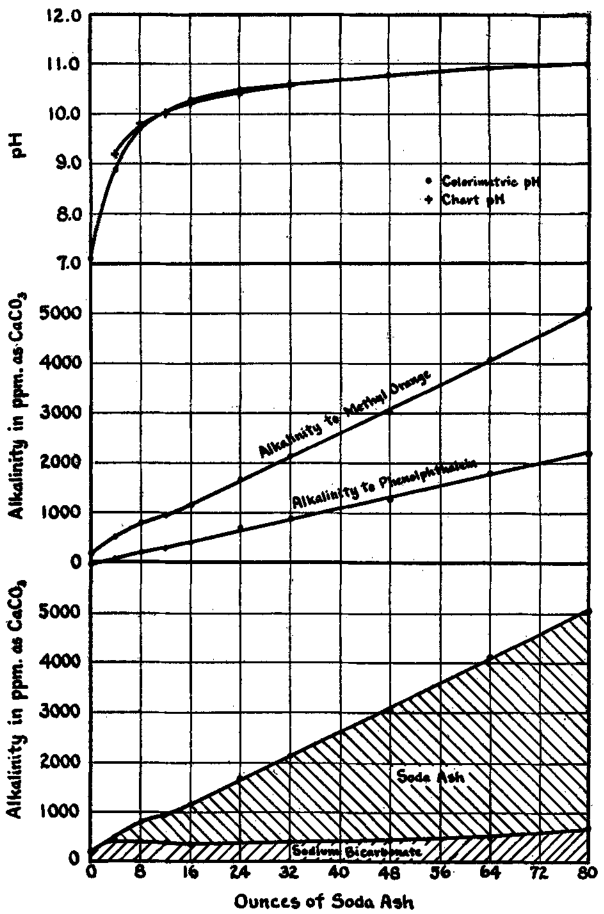

Chart II. Soda Ash on Family Work.

fabrics are highly resistant to alkalies. The solvent effects of alkalies on many types of soil might be greatly increased by increasing the pH. Likewise, it is evident from practice that the detergency of soap solutions increase with pH.

As a whole, the most promising field of study involves the intelligent exploration of the effects of alkalies in the washing formula to not only determine, if possible, to what extent the increased chemical effects of alkalies could be used to reduce the effects of more destructive factors, but also to make a comparison of the alkalies now available to determine their effective pH ranges and whether or not they have any individual specific properties that make them desirable.

This paper covers the results ot the first phase of an investigation that includes a comparison of alkalies as applied to the regular run of laundry work to determine the nature of soil from a viewpoint of its buffer or neutralizing effect on the several alkalies.

Method of Testing

To measure the neutralizing or buffer effect of soil on alkalies, approximately uniform weight lots of soiled clothes were loaded into a regular cylinder washer and a measured quantity of soft water was added. The machine was run for five minutes to dissolve any readily soluble soil that might be present. Without draining or stopping the machine a small sample of the solution was withdrawn through a small valve. There was then added a predetermined quantity of alkali and after five minutes another sample was withdrawn. This was repeated until the total intended quantity of alkali was added and a complete set of samples was collected. The machine was then drained and turned over to the regular operator to continue with his standard formula.

The collected samples were then titrated with a standard acid solution to the customary phenolphthalein and methyl orange endpoints, reporting each determination in parts per million of alkalinity present and in terms of the calcium carbonate equivalent value. Hydrogen-ion determinations were also made with the W. A. Taylor colorimetric comparator and the pH values reported. Another set of pH values were estimated from the titration results by means of a chart previously published.* Since considerable variations in soil conditions were known to exist in what seemed to be the same type of loads all reported values are the average of at least four loads. The charts to follow are in effect titration curves of loads of dirty clothes since the procedure was merely the indirect titration of the soil on a rather large scale.

Caustic Soda

With regular loads of damp wash, rough dry and shirts averaging 166 lbs., loaded in a 10-pocket 42-in. by 84-in. metal washer to which was added an average of 120 gallons of water measured by a Chace measuring valve, the first series of eighteen loads were run with caustic soda using a total of 12 ounces to the

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*Kansas Laundry Owners and Workers Short Courses, 1934. P. 57. Also Laundry Age, Sept., 1935, under title of "Know Your Washroom."

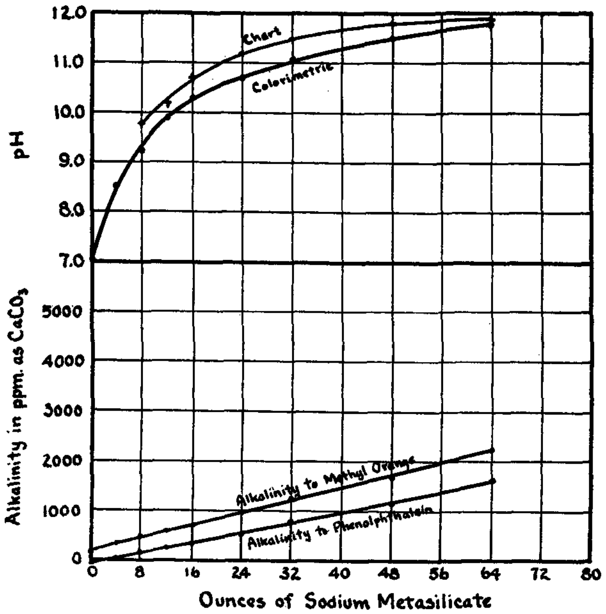

Chart III. Sodium Metasilicate on Family Work.

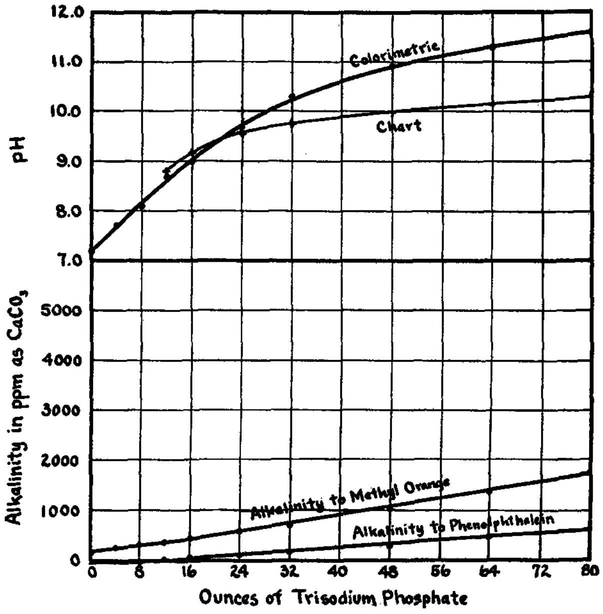

Chart IV. Trisodium Phosphate on Family Work.

load. The zeolite softened water supply had a phenolphthalein alkalinity of 0, a methyl orange alkalinity of 120 p.p.m. and a pH of 7.6. The average results of the tests are shown on Chart I.

The initial sample, representative of what was dissolved from the load with the application of water only, showed a drop in pH from the original water at pH 7.6 to a pH 7.3 (upper curve). Likewise from a water with titration values of Pht. 0, M.O. 120, the soluble matter changed these values to a negative phenolphthalein value (back-titration) of 30 ppm. and an M.O. of 220 ppm. (center curves). Thus a small amount of neutral buffering material has been dissolved from the load and shows up as titratable (back) to phenolphthalein and to methyl orange. The first ounce of caustic soda is almost completely lost in the titration results while the second ounce produces a measurable phenolphthalein alkalinity. After the third ounce the titration curves become nearly straight line functions. Meanwhile the pH values have risen regularly with the estimated chart results closely paralleling the colorimetric results.

At a point where the phenolphthalein alkalinity is one-half the methyl orange alkalinity (approximately 6.2 ounces) the titration value is representative of soda ash or its equivalence insofar as titratable alkalinity is concerned. Thus it has required over six ounces of caustic soda to, in effect, produce soda ash in the wash-wheel. Beyond this point the titration results suggest free caustic in addition to the soda ash.

In the lower section of the chart certain liberties have been taken with the data at hand for purposes of illustration. Of the initial methyl orange alkalinity, 120 ppm. is known to be represented by the sodium bicarbonate in the softened water. The balance represents the unknown buffer material from the clothes. No effort was made to identify it. For the chart we have called the entire quantity sodium bicarbonate, meaning either this or its equivalent in the titration. When the phenolphthalein alkalinity approaches a positive value at about the 1.5 ounce point, we reach the maximum bicarbonate value. Thereafter we might assume that the bicarbonate is being converted to carbonate. Part of it really is, while the unknown material is likewise being converted to a more alkaline substance. In graphical form there is illustrated the conversion of bicarbonate to carbonate by the addition of caustic soda. The carbonate or soda ash finally reaches a fixed point after which the additional caustic soda is indicated as such.

Thus there has been rather crudely shown in an empirical way what has happened to the caustic alkali that was added to the load. A calculated 1.6 oz. reacted with the bicarbonate in the water. About 4.6 oz. reacted with the soil in the clothes while the excess beyond this can still be located as an excess present as free caustic. Many other interesting facts can be interpreted from these curves by further study.

Non-Caustic Alkalies

Using exactly the same methods as with caustic soda a series of loads were run with soda ash using larger unit additions and a total of 5 lbs. instead of 12 oz. in order to reach a reasonably high alkalinity. With the exception of the pH scale the curves of Chart II are plotted on a different scale of values in order to keep down the size since the titration results assume enormous values as compared to caustic soda. It may be noted that after a rather abrupt rise the pH curve levels off and only reaches pH 11.0. In the lower section of the chart the ever present sodium bicarbonate (and soil), which in this case is not converted, acts as an efficient buffer throughout. In fact it is too efficient if high alkalinities are anticipated. Measured by pH values alone it takes three times as much soda ash to reach pH 10.0, 5 times to reach pH 10.5 and 13 times to reach pH 11.0. It is evident that soda ash alone is not very practical if high alkalinities are to be expected.

Chart III represents a series of loads with sodium metasilicate (pentahydrate). Because of a lower total sodium oxide value the titration values are smaller than with soda ash. The colorimetric pH curve indicates that with sufficient quantities higher pH values can be reached which in turn indicates that while the total alkali

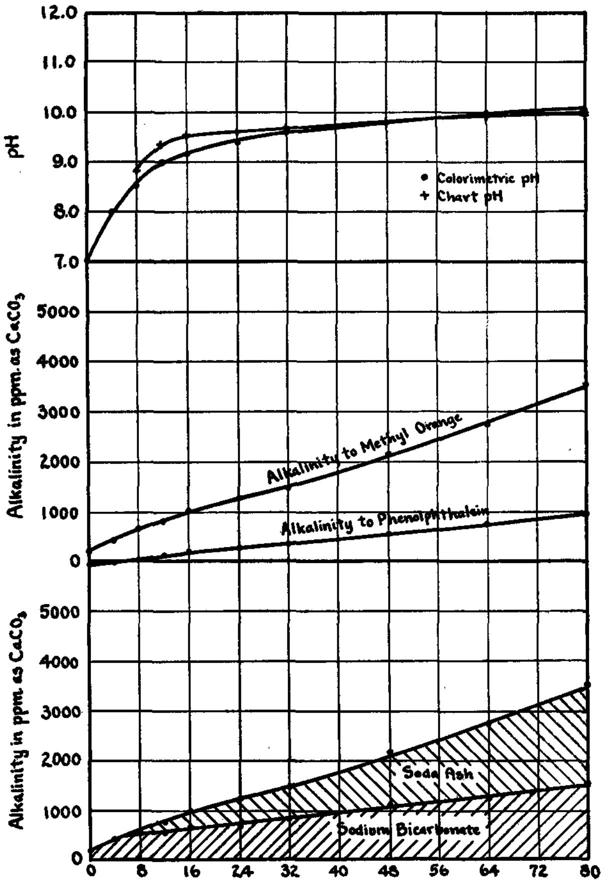

Chart V. Modified Soda on Family Work.

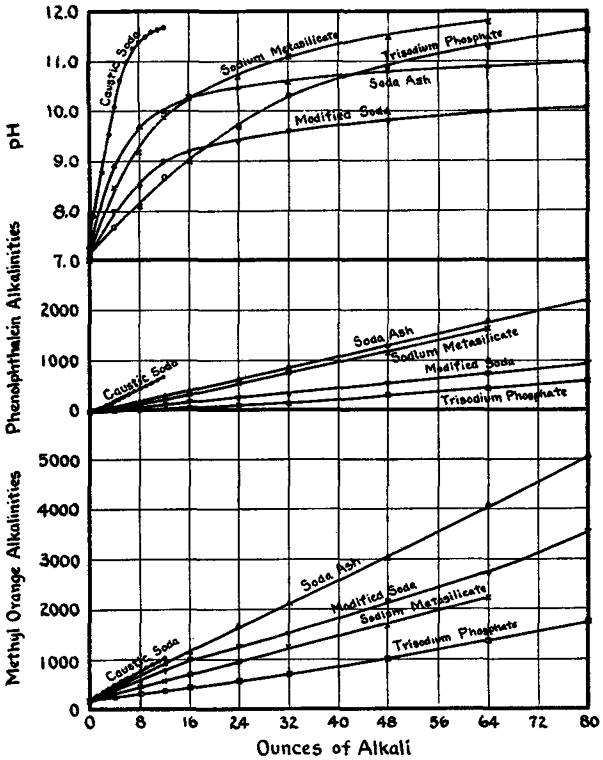

Chart VI. Comparison of Alkalies on Family Work.

content of this material is smaller the so-called active content is quite pronounced. Since the titration method employed was originally devised for carbonates and since metasilicate gives proportionately high phenolphthalein titration values because of the shape of its own neutralization curve the pH estimates from the chart (designed only for carbonates) are abnormally high and hence in error. The curve is included to illustrate this point. An illustrated division of titratable alkalinity between the sodium bicarbonate type of alkali and the silicate is not included as it would involve too much of a supposition on the type of silicate present. From the pH values when small amounts of metasilicate have been added it is evident that in the more dilute solutions the silicate is actually present as a lower-ratio less-alkaline silicate that approaches but never reaches a ratio equal to metasilicate.

In Chart IV trisodium phosphate (hydrated) exhibits a different type of curve. Titration values are low as is typical of the product while the pH values rise less abruptly than the previous alkalies but ultimately exceed soda ash. Estimated pH values from the chart are abnormally low in this case because of the proportionately low phenolphthalein alkalinity even at high pH values. No effort has been made to proportion off the bicarbonate and the phosphates since the titration values in this case are not representative of such a division.

Chart V illustrates another set of loads run with modified soda. Since this type of product is already a buffer mixture of sodium carbonate and sodium bicarbonate the shape of the curves are easily understood. A pH of 10.1 is the maximum reached in the tests even though titration values were rather large. The nature of this product limits its use to conditions where high alkalinities are not desired.

Chart VI is a composite of the previous five charts showing only the colorimetric pH value and titration values. Here the marked difference in the behavior of caustic soda is more pronounced as all products are charted on the same scale. Comparison of relative quantities of the various alkalies

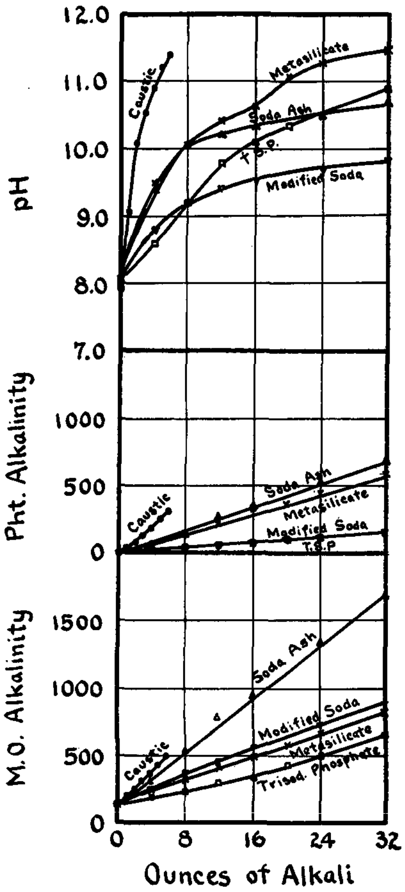

Chart VII. Comparison of Alkalies on Hotel Flat Work.

required to reach given pH values can be made and on this basis alone alkalies might be evaluated, although many other factors may enter into their ultimate values as soap builders. While some differences in load conditions may have existed the average of a number of loads in each case should equalize the results so that they are readily comparable. Different water conditions will modify the pH values attained with the specific quantities of alkalies indicated. Likewise load sizes and soil conditions are highly important points.

This latter point is illustrated in Chart VII. Hotel flat-work, bath towels, etc., were run in loads averaging between 275 to 300 pounds in a 42-in. by 84-in. metal washer using a 3-in. water level as measured by a float-type gauge. As this work was relatively clean, lesser amounts of alkalies were added. Only three loads were run with each alkali and since considerable variation existed in the types of loads the comparative results may not be as accurate as in the case of the previous chart. The relative cleanness of this work as represented by the low buffer effects is evident by the lesser amounts of alkali required to reach specified pH values even though the loads were almost twice as large..

Discussion of Results

This preliminary investigation indicates to a degree the extent of the buffering material present in typical loads of soiled clothes and the extent to which alkalies are buffered by the soil. A comparison has been drawn between a number of common alkalies with some suggestion as to the limitation of some of the products if higher alkalinities are desired.

Since actual studies of soil removal have not been included in this paper, no suggestions are offered relative to the optimum pH or choice of alkali. It is hoped that these conclusions may be reached or at least more definitely approached by further work now in progress.

Acknowledgment

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THE CHEMISTRY OF PHOSPHATIDES AND THEIR UTILIZATION IN INDUSTRY

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THE term phosphatides is used interchangeably with phospholipins and includes the lipoids or fat-like compounds which contain phosphorus. All these substances are comparatively unstable and are autoxidizable, thus making their study very difficult, and always introducing the possibility that the compound finally found was not the one originally present. Further, the different phosphatides are highly inter-soluble, making them difficult to separate even when solvents are available that differentiate accurately the pure substances.

The two most commonly known phosphatides are lecithin and cephalin, of which cephalin is the less stable and accordingly less easily studied and less completely understood. They may be considered respectively the choline and the aminoethyl alcohol esters of phosphatidic acid. Phosphatidic acid is the name used by Chibnall and Channon (1927) to describe a tri-glyceride in which one fatty acid radical is replaced by phosphoric acid.

Lecithin and cephalin are ordinarily considered generic terms to the extent of including compounds containing different fatty acid groups. Thus, stearyl-oleyl lecithin is usually considered the chief lecithin present in eggs; yeast is said to contain palmytyl-oleyl and dioleyl lecithin, and in brain and similar tissues, lecithins containing more highly unsaturated acids, as linoleic, linolenic, and arachidonic, predominate.

The term lecithin is sometimes, however, applied on the basis of solubility. Lecithin is soluble in alcohol and ether, but insoluble in acetone; cephalin soluble in ether but insoluble in alcohol and acetone. Thus, phosphatides with nitrogen bases other than choline, as neurine and betaine, have been called lecithins by many authors, and especially in the case of plant materials, compounds known to contain sugars are very commonly called lecithins. In some of the latter cases the carbohydrates have been considered to be merely adsorbed impurities that could not be removed because the amount of material available was too small for a sufficiently extended series of reprecipitations. In other cases the phosphatide is called lecithin from its solubility even though the sugar is considered to be a part of the molecule. From brain tissues lipins have been isolated which appeared to be a combination of glycolipin with phospholipin, united by an oxidized sulfur atom, and accordingly named sulpholipins or sulfphatides. In some plant materials glycophospholipins seem to occur without any sulfur.

The standard classifications of proteins contain the group lecithoproteins. Our knowledge of these compounds is exceedingly meager, but indirect evidence indicates that a large proportion of the lecithin both in animal tissues and in plant seeds is in combination with protein. For instance, ether alone extracts from ground wheat a small amount of phosphatide, but if the wheat be first treated with alcohol, ether will extract about four times as much phosphatide, even though the alcohol were evaporated in place without removing any material. Furthermore, if a dough be made of flour and water with 0.001 per cent pepsin and allowed to stand for two hours, then dried, ground, and extracted with ether alone, more than twice as much phosphatide is

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[1]Contribution No. 52, Department of Milling Industry.