

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 sug-

gestion 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.

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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 ordi-

narily 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 dioleoyl 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 sulphatides. In some plant materials glycopospholipins 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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extracted as from similar dough without the pepsin.

Of great interest are the publications of A. C. Chibnall and various co-workers (1927 et seq.) reporting that in leaf cytoplasm from various sources they found no phosphatides such as lecithin or cephalin containing nitrogen bases but only calcium phosphatide, which was completely soluble in ether without previous treatment with alcohol. It is suggested by these authors that this is an intermediate step in the synthesis of lecithin. The sodium or potassium salts of phosphatidic acid are soluble in water, and so could be transported to storage organs where esterification with choline or other nitrogen bases would form the phosphatides such as lecithin and cephalin. This is a very attractive theory but requires careful checking. The most surprising point is that no lecithin at all was found, while later work by Smith and Chibnall (1932) and Jordan and Chibnall (1933), showed much lecithin, and in actively growing yeast the very careful work of Daubney and Maclean (1927) showed lecithin and cephalin, but no indication of a phosphatide containing no nitrogen base.

Functions of the Phosphatides

Phosphatides are apparently present in every living cell and accordingly are usually assumed to be indispensable. Their ease of oxidation, a reaction which is apparently reversible within the cell, has suggested that they may be instrumental in the process of respiration. Palladin (1910) and Gallagher (1923) have collected considerable evidence in support of such a theory, but absolute proof is still elusive. Even the changes occurring in lecithin on oxidation are not entirely clear. It is usually assumed that oxidation first occurs at the double bond of the unsaturated fatty acid, and this seems to be the case in vitro with pure lecithin. However, MacLean (1927) reports that if tissues to be extracted are not dried as quickly as possible, the percentage of lecithin is decreased and that of cephalin increased, and the author has found a higher proportion of cephalin in bleached flour than in unbleached. These observations indicate an oxidation of the nitrogen base rather than the unsaturated acid.

The great reduction of the surface tension of aqueous media by lecithin led to the assumption that

it would concentrate at the cell wall and the theory was proposed that a plasmatic surface layer consisting in part of lecithin controlled the entrance and egress of materials, the entrance of fat soluble dyes and anaesthetics being held possible only through the presence of the lipoid. Recent plant physiologists, as typified by Steward (1929), having found serious errors in the original theory, have probably gone as much too far in the opposite direction by denying to the phosphatides any important role in the control of the intake of the cell.

Instead of appearing only in the surface layer of the cell, the phosphatides appear to be distributed throughout the cytoplasm of the cell, coating at least in part the individual protein aggregates. This interpretation is supported by the observation of Working (1924, 1928) that phosphatides, both those originally present in the flour, and any that may be added in making the dough, have an important effect on the plastic and elastic properties of the gluten. Similar results are reported for blood fibrin by A. P. Mathews (private communication). Such uniform distribution of the phosphatide throughout the cell protoplasm does not in any way reduce its importance in modifying the absorption characteristics of the cell, and makes even more easily understood the entrance of fat-soluble substances into all portions of the cell.

An investigation by the author into certain obscure changes in the physical properties of dough from wheat flour brought out the fact that a dispersoid of lecithin in water is rapidly flocculated by oleic or linoleic acid. Certain of the saturated acids low enough in the series to have some solubility in water seem to have a similar action. This reaction appears to be more in the nature of an adsorption rather than a chemical combination since no definite stoichiometric relation could be observed, but the effective result is the same, and might be described as a "water-proofing" of the hydrophilic portion of the lecithin molecule.

Phosphatides in Industry

The chief uses of phosphatides in industry may be considered as depending upon three properties, first, their emulsifying action, due at least largely to their reduction of the surface tension of water; second, their tendency to adsorb, forming surface films upon solid or semi-solid parti-

cles whether in aqueous or fatty media; and third, their anti-oxidative action. It may seem strange that a substance which is itself actively autoxidizable when added in very small proportions to an oil or fat should protect the latter from oxidation over long periods of time, but it is nevertheless the fact, as shown by the prolonged holding of treated and untreated fats under normal storage conditions. It is to be observed, however, that phosphatides will in no case give satisfactory results in accelerated oxidation tests where high temperatures are used, such as those in the range of the boiling point of water. Some measurements of the antioxidant properties of phosphatides have been made by Evans (1935).

In Europe there is a very wide use of phosphatides in the manufacture of margarine, and some use has been made of them in this country. Since many of the properties of butter are due to the presence of lecithin rather than that of milk curd, the value of the addition of phosphatides can be understood, and in some cases fats can be chosen which contain small amounts of phosphatide. One of the most notable effects seems to be the better retention of moisture and salt on standing. In margarines without lecithin there is a marked tendency for the water to drain out and evaporate leaving the salt on the wrapper instead of in the margarine. Excessive salt on the surface of the margarine or the collection of globules of brine in the interior is also likely to make the margarine taste as though it were too highly salted.

Phosphatides also seem to have the effect of making the different fats more completely inter-soluble, or perhaps of dispersing those of higher melting point more thoroughly in the others, retaining a more butter-like consistency. This consistency is commonly translated by the tactile nerves of the mouth and throat as a taste. The advantages of the phosphatides are more clearly noticeable in margarines made largely from coconut and palm nut oils, and as these approach most closely to butter in the nature of their fatty acids, the combination produces margarines of unusually desirable characteristics.

Phosphatides are being used to a considerable extent in the chocolate industry. The advantages appear to lie in a greater inter-solubility or a better dispersion of the fats of different melting points, and a strong

adsorption of the lipin to the solid particles. Possibly the affinity of the phosphatides for water is also of importance.

In certain phases of candy making where fats are added to sugar mixtures, the use of lecithin has appeared to give better distribution and utilization of the fats, even though butter, which already contains some natural phosphatide, is the fat used.

The baking industry has long used ingredients whose effect is due partly or largely to their lecithin content, but the use of purified phosphatides is not yet sufficiently understood to have come into extensive use. In the use of eggs in cake the egg protein is of major importance, but whenever the egg yolk is used, the lecithin it contains modifies greatly the physical properties of the proteins.

In the case of breadstuffs leavened by yeast, the phosphatide present in the flour itself apparently has an important effect in modifying the gluten characteristics. In this type of baked goods, when egg is added, practically its entire effect is due to the lecithin contained, and when buttermilk is used, a large part of the effect is due to

the lecithin. In this case the acid contained also has an important action on the physical characteristics of the dough.

In treating leather with oil to preserve its pliability, and especially to restore pliability and good appearance after cleaning with organic solvents, the addition of phosphatide to the oil seems to be of considerable value. The reasons for this have not been sufficiently studied, but the anti-oxidant properties may be important, as well as the tendency to adsorb on protein surfaces.

The cleaning properties of dry-cleaning preparations and of ordinary soaps seem to be enhanced, at least in some cases, by the addition of phosphatides, and advantages are especially apparent in super-fatted soaps.

Phosphatides appear to effect a marked improvement in the spinning properties of cellulose esters, and may also show value as plasticisers in lacquers and varnishes. In the latter case, however, their affinity for water limits their usefulness.

Finer emulsification in certain cosmetic preparations, and better spreading and clinging properties

in oils used for medicated nasal sprays have been observed as resulting from the use of phosphatides.

A great increase in the industrial uses of phosphatides in this country may be expected with the development in this country of plants for their production from soy beans.

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LIST OF A. O. C. S. REFEREE CHEMISTS FOR 1936-37

The following have certificates reading on analyses of all cottonseed products and similar materials covered by the methods of the A. O. C. S.:

- | | | |
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| G. K. Witmer, The Battle Laboratories, Inc., Montgomery, Ala. | R. M. Simpson, Chas. W. Rice & Co., Columbia, S. C. | R. H. Fash and F. B. Porter, The Fort Worth Laboratories, Fort Worth, Texas. |
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The following have certificates reading on analyses of cottonseed, cake and meal:

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The following have certificates reading on cake, meal, fatty oils, and soap stock:

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