phosphates since they hydrolyze ultimately to orthophosphates. They have been used extensively as water softeners. The insoluble Maddrell's salt has been tested sufficiently to allow its use as an abrasive in tooth powders.

Their usefulness may be expected to be limited by several considerations: 1) Interference of orthophosphates and probably of other ions, 2) Hydrolysis of metaphosphates through pyro to orthophosphate. The hydrolysis is accelerated by heat, acid, and alkaline earth metals, particularly calcium in foods. In this connection it should be mentioned that solutions of "hexametaphosphate" and Maddrell's salt, adjusted to pH 7.5 were kept several months in a refrigerator without noticeable loss of antioxidant activity. Also these compounds showed high antioxidant activity in experiments with heated muscle extracts extending over many weeks at 45° (5).

Summary and Conclusions

The antioxidant activities of a number of synergists were measured in aqueous fat systems at several pH values. A group of polyphosphates not previously investigated was most promising of the synergists tried. Orthophosphates were ineffective but antioxidant activity increased from pyrophosphate through tri and "heptaphosphate" and finally to the most active "hexametaphosphate" and Maddrell's salt. Citrate compared with triphosphate and pyrophosphate in antioxidant activity; all other synergists tried were less effective than pyrophosphate.

Relatively large molar concentrations of orthophosphates interfered markedly with the antioxidant activity of citrate and the higher polyphosphates.

The polyphosphates also inhibited rancidity in the presence of added copper and iron but did not eliminate the catalytic effect of the metals.

Antioxidant activity of the phosphates in dry fats did not parallel their activity in aqueous fat systems.

Properties of polyphosphates which might affect their use as antioxidants in foods are discussed.

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Solvent Extraction. II. The Soaking Theory of Extraction[1]

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THE study of extraction of crude lipids from vegetable oil-bearing materials for application of the data to equipment design or process control makes apparent the need for a clearer understanding of the mechanism by which oil transfers from the solid to the liquid or miscella phase. In spite of the extensive application of solvent extraction, particularly in the soybean processing industry, there is no universally accepted concept of the manner in which the basic process occurs. The problem is reviewed briefly by Karnofsky (2). The present paper extends our knowledge of the subject but is not a complete answer.

Oil-bearing seeds that are usually prepared in the form of flakes or grits for the extraction process have a porous structure. King (1) has established the volumetric composition of a raw soybean flake to be 51% dry solid, 8% water, 22% oil, and 19% air. Where porous materials are being extracted, the theory of diffusion may be expected to apply, and the data should conform with theoretically derived equations for diffusion.

Extraction of soybean oil from porous clay plates does conform to theory as proved by Boucher (5). King demonstrated that data for the extraction of oil from soybean flakes fail to conform (1). Osborn (3) applied the concept of two parallel structures, one permitting fast extraction and the other slow, and obtained a better agreement with the diffusion theory. However the application of this concept to present data required the assumption of more than two structures. This involves complications that limit the usefulness of the concept in commercial design.

An oil-bearing substance such as a flake, is composed of four parts: 1. non-oil-bearing solids, 2. water, 3. oil, and 4. air space as illustrated in Figure I. For the purpose of this discussion the non-oil-bearing solids and water are treated as a single

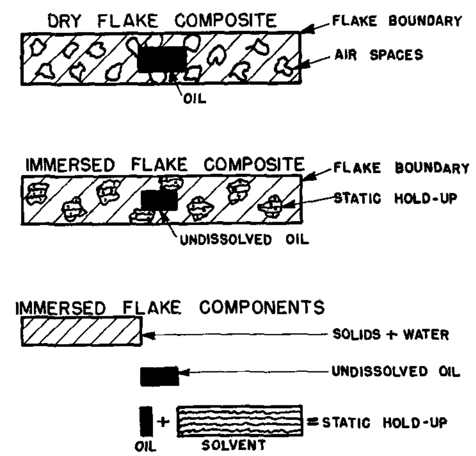

FIGURE I

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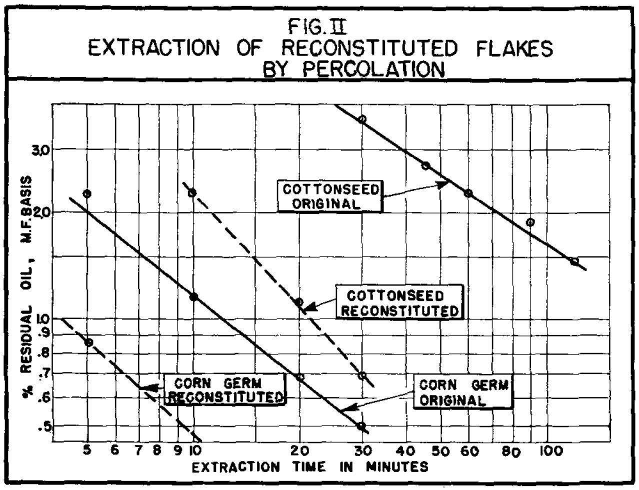


FIG. II
EXTRACTION OF RECONSTITUTED FLAKES BY PERCOLATION

component. When the flake is immersed, the air space is filled with liquid of the composition of the surrounding solution. As extraction proceeds, the space originally occupied by the oil is also filled with this liquid. This void-filling solution is termed "static holdup," meaning that it is held within the boundaries of the flake and will not drain. The data of King demonstrate that this amount of liquid remains even under the action of mild centrifuging (1).

The oil in the flake under extracting conditions is considered to exist in two parts. One part is a component of the static holdup and is influenced by the concentration of the surrounding solution. The other part is the portion of the original oil content that has not yet been transferred from the solid to the solution. This latter is termed "undissolved oil." The completely-drained extracted meal from any extraction process after desolventizing has an oil content that is the sum of these two parts. This concept may not agree with the actual physical disposition of oil in the flake structure, but it has been found useful in treating extraction data for commercial design.

A LARGE quantity of data on extraction rates has been collected in the laboratory by the two methods previously published (4). These methods, the "Percolation Method" and the "Batch Co-Current Method," were designed to study the extraction of undissolved oil under the two basic means of contacting solids and liquids, i.e., 1. percolation of the liquid through a stationary column of solids and 2. the immersion of the solids in a body of liquid.

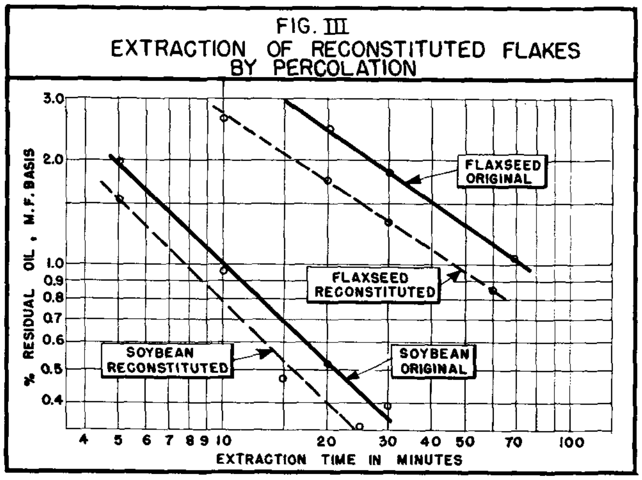


FIG. III
EXTRACTION OF RECONSTITUTED FLAKES BY PERCOLATION

In the percolation method a continual flow of fresh solvent is maintained through the bed. The effluent is collected at successive time intervals, the miscella is desolventized, and the residual oil in the meal at each time interval is calculated from the oil quantities. The data are then plotted on log-log paper to relate the percentage of residual oil in the meal to the total time of extraction.

In the batch co-current method the sample is stirred in a batch of solvent and samples of miscella are withdrawn at time intervals for analysis of oil content. The difference between the total oil in the sample and the oil calculated to be in the miscella is termed "undissolved oil." This value is plotted against total time of extraction. Treatment of data from the batch co-current method involves the concept of undissolved oil and static holdup that is illustrated in Figure I.

The difference in extracting conditions of the batch co-current method and the percolating method are evident from a consideration of the operating technique and the analyses given in Figure I. In the first case the static holdup is momentarily pure solvent (or the concentration of the initial extracting solution) but rapidly builds in concentration approaching some equilibrium value. Hence the undissolved oil is decreasing with time, but the oil concentration of the static holdup is increasing. In the percolation method it can be assumed that the static holdup is essentially pure solvent for all but the first few minutes of the extraction because of the relatively high rate of solvent flow and the shallow depth of bed.

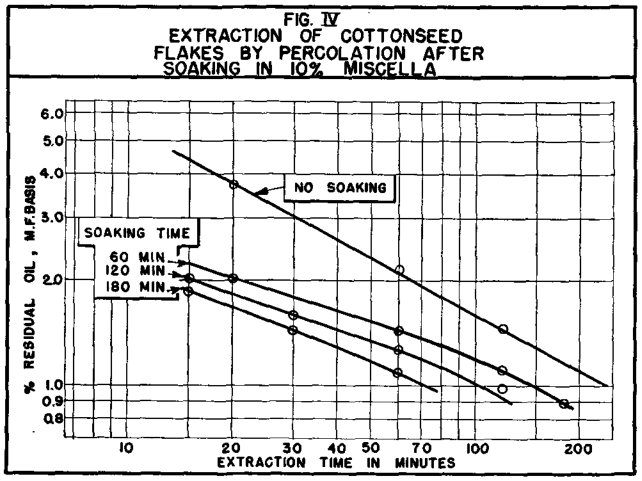
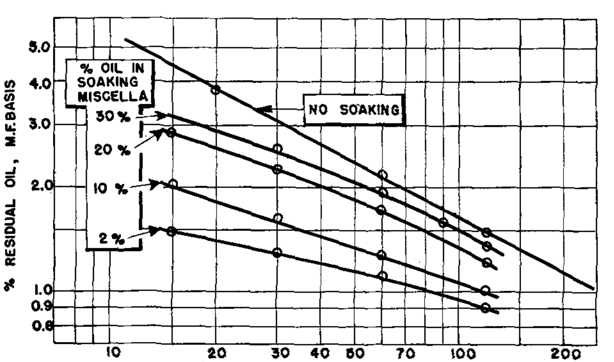


FIG. IV
EXTRACTION OF COTTONSEED FLAKES BY PERCOLATION AFTER SOAKING IN 10% MISCELLA

In spite of widely differing conditions of concentration, identical results have been obtained from both methods for concentration of miscella up to 10% oil in commercial hexane. This does not agree with the diffusion concept. It can be explained on the assumption that the oil is bound in the original substance through a resistance that is slowly soluble. Since glycerides are not slowly soluble in hexane, the slow solution rate may be due to the presence of phosphatides and other minor components which have limited solubility and become more effective by their higher concentration in the last of the oil extraction (6).

If this is so, it can be expected that, if the oil is first extracted from the seed, replaced in the seed, and again extracted, it should be removed at a faster

FIG. V
EXTRACTION OF COTTONSEED FLAKES BY PERCOLATION AFTER SOAKING FOR 120 MINUTES



rate the second time. If structure were the controlling factor, the extraction of the reconstituted flakes should duplicate the original extraction. Cottonseed, corn germ, flaxseed, and corn germ flakes were extracted by the percolation method with commercial hexane to 1% residual oil or less, the desolventized extracted oil replaced on the solids, and the reconstituted germ again extracted. The extraction data are given in Figures II and III. In every case there was a considerable increase in extraction rate for the reconstituted flakes. Evidently the original resistance is not remade when the flakes are reconstituted.

An extension of the undissolved oil concept involves the evaluation of soaking alone as an effective extracting force. If the oil extracts mainly under the action of time, merely steeping or soaking the solids in miscella should contribute to the transfer of oil from the solid to the liquid phase. Because of the interest in the effect of soaking on the performance of a percolation-type extractor, a series of experiments was undertaken in which soaking preceded percolation. In Figure IV are shown the results of soaking a sample of cottonseed flakes in 10% miscella for various lengths of time and then extracting by the percolation method. Soaking and extraction were conducted with commercial hexane at its boiling point. It is evident that soaking contributed greatly to the extractability of the flakes and the improvement was greater with longer time.

In another set of experiments the sample was soaked in different miscella concentrations for 120 minutes. Then they were extracted by percolation. The results in Figure V indicate that soaking in all strengths of miscella contributes to the extraction, but the more dilute miscellas are the more effective.

A quantitative measure of soaking as an effective mechanism is shown by comparing the total time of soaking plus percolating with the time required by straight percolation to reduce the residual oil to 1%.

TABLE I

Extraction of Cottonseed Flakes With Commercial Hexane by Percolation After Soaking

% Oil in Soaking Miscella	Time in Minutes			Time to 1% Residual Without Soaking
	Soaking	Percolation to 1% Residual	Total	
2	120	80	200	230
10	60	145	205	230
10	120	100	220	230
10	180	70	250	230
20	120	155	275	230
30	120	200	320	230

The data from Figures IV and V are listed in Table I. Soaking in 2% miscella actually decreased the time required to reach 1%. The data for 10% miscella indicate that, up to a point, soaking is just as effective as percolating. The conclusion from these data and fortified by other data not given here is that soaking in any concentration below 20% for half the total time required to reduce the residual oil to 1% is just as effective as percolating time with fresh solvent. A practical conclusion from this observation is that the concurrent side of a basket extractor is almost as effective as the counter-current side.

Summary

The extraction process within the oil-bearing substance is described in terms of undissolved oil and static holdup. Undissolved oil is bound in the original material through a slowly soluble resistance that is not re-established by replacing the extracted oil. The rate of solution of the oil is relatively independent of the concentration of the extracting solution and is mainly a matter of soaking time. Soaking in any concentration of miscella below 20% for half the total extraction time required to reduce the undissolved oil to 1% is just as effective as extraction for the entire time with fresh solvent.

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