

reality our sub-neat to neat transition, although it seems hardly likely that earlier workers failed to distinguish between melting to form liquid crystalline neat soap on the one hand and melting to form isotropic nigre on the other.

ACKNOWLEDGMENT

The authors are very heavily indebted to Dr. A. S. Richardson of this laboratory, under whose direction the work was initiated and carried out. His assistance is also gratefully acknowledged in the interpretation and presentation of the experimental results, upon which this paper is based.

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 (8) A.S.C. Lawrence Trans. Farad. Soc. 34, 660, (1938). The figures given in Table V refer to sodium palmitate monohydrate. If the samples were prepared, as would be inferred, by drying the soap to constant weight at temperatures just above 100° C., anhydrous soap would result.
 (9) See Thiessen & Stauff. Z. phys. Chem. A176, 397 (1936), (and previous papers). These authors believe that certain "genotypical" transformations occur within the solid soap at temperatures well below 100° C. Our experience indicates that these changes are relatively small compared with the phase changes discussed herein.
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Table I.
Dilatometric Data for Sodium Palmitate.

Temperature (° C.)	Heating	Cooling	Temperature (° C.)	Heating	Cooling
90	-72.0		193		
95	-61.5		194.5	261.5	
100	-50.5		195	263.0	
105	-38.5		196	(265.0	
110	-28.0			to 269.0)	
115	-18.5		197	(307.0	315.5
		(+10.0 to -8.5)		to 309.0)	
116	-16.0		200		322.5
117	-12.5		202	326.0	
119	(+21.5 to +29.0)	+24.0	204	331.0	
120	45.0		206	335.5	
122	50.5		208	340.5	
125	57.5		210	345.5	346.5
130	67.5		211		348.5
132	73.5		212	350.0	
134	81.0		214	355.0	
135	86.0		215		359.0
		(124.0 to 113.5)	216	360.0	360.5
136	(90.0 to 101.0)	125.5	217	362.5	
			218	365.5	
140		136.0	220	369.5	370.5
150		156.0	225	380.5	
152		159.5	230	391.0	391.5
156.5	168.0		234.5	402.5	
160	175.0		239.5	413.0	412.0
162	178.5		242		417.5
164		178.5	245	426.5	
165		183.0	249		434.5
		(190.0 to 186.0)	251	439.0	439.5
166		(191.5)	253	444.5	445.0
167	188.0		254.5	449.0	
168	(190.5)	199.5		to (450.5)	459.5
170		204.5	255.5	459.0	464.0
172	208.0		257.5	464.0	464.0
174	213.0		261.5	474.0	
176	215.5	(223)	266.5	488.5	
177.5	(220.0 to 222.5)		272	501.5	501.5
			277	515.5	
178		228.5	282.5		530.0
180	232.0	228.5	286	540.0	
182	236.5	232.5	288		545.5
184	240.7		291.5	554.0	552.5
185		243.0	293.5	559.5	558.5
186	245.0		294.5		562.0
188	249.0		295.5		570.5
190	253.5		297		574.0
192	257.0		299	580.0	580.5
			304.5	593.5	

* The dilatometer readings represent the distance of the mercury meniscus from a fixed reference point. These readings are directly proportional to the volume of the soap and could be converted to a volume basis by using capillary calibration, and corrections for the mercury, the dilatometer volume, etc. () represents points in a state of adjustment to the stable equilibrium curve.

LECITHIN-Its Manufacture and Use in the Fat and Oil Industry

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Abstract

Lecithin, produced economically and on a commercial scale from soybeans, has been on the market in this country only since 1929. The lecithin and associated phosphatides are extracted with a petroleum solvent and separated mechanically from the mass of oil. Special grades may be prepared by subjecting to further solvent purification and fractional crystallization. In the fat and oil industry the properties of lecithin are used to inhibit rancidification and to modify interfacial tension relationships. Quantities used range from .01% to 1.0%. Various applications are noted as in oleomargarine, shortenings, confections, coatings and icings, vitamin oils and for industrial purposes.

useful commodity, available in quantity, is of recent date. And this transition waited upon recognition of the natural connection between lecithin and the production of edible oils¹, for essentially lecithin is a close relative of ordinary oils and fats. Indeed, lecithin is a tri-glyceride except for substitution of one of the fatty acid radicals by phosphoric acid combined with a nitrogen containing base².

For years the term "lecithin" was used inclusively. The broader term is "phosphatide" and from a strictly technical standpoint lecithin is that alcohol soluble phosphatide containing the base choline. However, commercial lecithins have al-

ways consisted of mixtures of phosphatides³, especially lecithin and cephalin (alcohol insoluble, with amino-ethyl alcohol as the base) along with a carrier of oil and are still generally referred to in the trade as "lecithin." The commercial product may or may not contain an appreciable proportion of carbohydrate. The fatty acid radicals vary depending, for example, on the species of bean and the environment so that phosphatides from American grown beans will differ slightly from those of Manchurian origin. There is always one unsaturated fatty acid radical, however, which appears to

WHILE lecithin was first prepared many years ago from egg yolk and brain substance, its development from a laboratory curiosity and costly pharmaceutical into an industrially

play a major physiological role.

It follows that in analytical work the factor of 26 x P, used to calculate the purity of egg lecithin, should be applied relatively rather than literally to commercial vegetable lecithin. An analysis of oil-free soybean phosphatide, gave 3.1 total phosphorus, indicating a higher factor. However, egg lecithin as produced is often a mixture and not a pure chemical entity and even very highly purified egg lecithin may exhibit a tendency to become in part alcohol insoluble. For convenience the term "Lecithin" hereinafter refers to the soya-lecithin of commerce unless qualified by the context.

Depending upon the raw material and method of manufacture the free fatty acid content of lecithin products will vary but, to avoid an excessively high figure in any case, should not be determined by direct titration in the usual way. The lecithin and other phosphatides tend to react with the alkali. Besides saponifying more readily than ordinary oils and fats, lecithin contains a free acid hydroxyl in the phosphoric acid group⁴; cephalin in particular has somewhat of an "organic acid" character and is isoelectric at a pH of about 5. The free fatty acid should be run on the matter extracted by washing with an excess of cold acetone. Preliminary addition of a small amount of ether facilitates this operation; the acetone may be mixed in warm but the whole mass should be chilled to -15° C.

Probably the first to envisage the possibility of producing vegetable lecithin commercially from soybeans and to devise feasible processes and equipment was Hermann Bollmann of Hamburg. Bollmann concerned himself with solvent extraction. After the war soybeans were handled increasingly by the German oil mills and being relatively rich in lecithin afforded an excellent source for this substance. Bollmann originally used a combined solvent of about two parts alcohol and three parts benzol or a volatile liquid hydrocarbon on the theory that the residual meal would be more palatable⁵. Also this combined solvent gave a larger lecithin yield by loosening or breaking the lecithin-protein combination in the bean. The current of solvent moved counter to the direction of bean travel and a similar counter-current principle was employed in steaming the meal to remove traces of solvent⁶.

Conway and his associates in this country as early as 1923 appreciated the possibilities of solvent extraction including lecithin recovery, and negotiated with Bollmann for licenses under the latter's American patents. A pioneer plant was put under construction in Norfolk but for various reasons the project did not progress to regular commercial operation. This enterprise, however, gave impetus to the introduction of soya-lecithin as well as stimulated interest in the extraction of oil seeds. Since that time the domestic supply of soybeans has grown tremendously, centering in Illinois, and the past five years have seen solvent extraction become a large scale reality. Bollmann's methods for separation and purification of lecithin as an integral part of the extraction process are being successfully applied here as in Europe. Today, a single solvent derived from petroleum seems to be preferred to Bollmann's combined solvent⁷. Soybeans contain about 1½% to 3% of phosphatide but not all is removed during extraction so that the meal retains about 1%. While the single solvent does not afford as large a yield the refined lecithins are much freer from carbohydrates.

Before passing through the solvent the beans are cleaned, dried and flaked. The oil and lecithin dissolve out and after evaporation of the solvent moisture is introduced to hydrate the lecithin. It is then possible to effect a good separation with high speed centrifugals. The operation is continuous. A small proportion of oil remains "bound" to the lecithin, amounting to about 30% of the weight of the lecithin, and this later serves as a carrier.

The lecithin emulsion is subjected to vacuum distillation to drive off the water and this treatment also improves the taste and odor⁸. For certain purposes light colored grades are desired and bleaching with peroxides, for example hydrogen peroxide, effects a substantial reduction in the degree of red and yellow coloration⁹. The temperatures applied during processing do not prove injurious due to the protective presence of the oil and moisture. The carrier of soya oil in the finished lecithin guards against change of the active substance, which it renders soft and convenient to use.

Purified lecithin, free from oil, is waxy and gummy and less solu-

ble. The demand for this type comes chiefly from the pharmaceutical trade. The production cost is high. Less costly but still more expensive than the straight soya-lecithin are those grades which can be made by substituting some other oil or fat for soya oil as the carrier. For use in pure chocolate coatings, a purified grade with a cocoabutter carrier most fully answers trade requirements. The soya-lecithin after bleaching is washed with a selective solvent, usually acetone, in which the oil dissolves but the lecithin does not. The supernatant liquid is drawn off and the specified carrier, such as hydrogenated shortening or refined cocoanut whole oil, is mixed in. The residual solvent can then be evaporated¹⁰.

Commercial soya-lecithin can be split up into several closely related components by treating with alcohol, separating the residue insoluble at about 60° C. and subjecting the solution to fractional crystallization by cooling¹¹. So far no important commercial advantage or superiority has been found for any of the phosphatide fractions compared to the soya-lecithin obtained by the above described process which would justify the cost of separation. While it has been reported that highly purified cephalin is a more effective anti-oxidant than highly purified lecithin¹², it should be borne in mind that we are dealing with a natural extract, obtained by mechanical rather than chemical means. Indeed, for most purposes the natural lecithin-oil complex seems superior to the separated fractions and to a considerable extent the process of isolation may denature or change the original potency, even if the components should be later mixed back together in the same proportions. Nevertheless, future research will probably include a more detailed study of the individual vegetable phosphatides as well as of stable lecithin-protein combinations which might be used in acid media, as in mayonnaise^{13, 14}.

As early as 1924 Bollmann pointed out that ordinary refining and deodorizing methods destroy the lecithin naturally present in oils from seeds and that the addition of small fractions of a percent of lecithin to refined oils retards rancidity¹⁵. He observed too that in frying the oil did not squirt or spatter in the usual way. Lecithin is now widely used in various vegetable and animal oils and shorten-

ings to inhibit oxidation and rancidity, in quantities up to 0.15%. Continued use by the trade as well as many accelerated tests have shown its value as an anti-oxidant, and as would be expected the most striking results are obtained with the more unsaturated oils and fats. Beyond 0.15% the improvement is not proportionate and in some cases from 0.05% to 0.1% has been adequate^{16, 17}. It is interesting to note that in cod liver and halibut liver oil preparations vitamin potency is being prolonged by incorporation of soya-lecithin¹⁸.

Besides counteracting rancidity (and retarding hydrolysis¹⁹) lecithin, because of its colloidal effects, can be advantageously used in mixtures of different melting point fatty oils such as exemplified by compound shortenings²⁰, or in fats containing glyceride components of different melting points such as coconut oil products or cocoabutter. The lecithin, pre-mixed with part of the melted oils, should be added just prior to chilling. Lecithinated shortening exhibits greater physical stability, being less subject to "separation," "streaking" and "granulation." The fact that the mass of plasticized shortening is better adapted to bind the bubbles of air is evidenced indirectly by the foaming which occurs while testing in the Swift Stability Apparatus. On the other hand, the interfacial tension relative to water is reduced as indicated by smaller droplets when slices of potatoes are deep fried²¹.

Shortenings containing about 0.05% or more of lecithin darken very considerably during deep frying or on heating to elevated temperatures²². This may be ascribed to carbohydrate and perhaps indirectly to the phosphoric acid group in the lecithin molecule. Strangely enough with some compounds tested, but not all, the addition of 0.01% of lecithin resulted in a slightly lower Lovibond reading initially and did not increase the coloration after heating to 200° C. and frying potatoes. The control sample emitted a more pungent odor and during frying the bubbles were larger and less uniform. It is known, of course, that lecithin reduces interfacial tension between oils and water²³. Evidently the composition of the compound and the character of its oils and fats determines the maximum amount of lecithin which can be used where deep frying is a factor, so that a

series of tests should be made for each formula.

Just as lecithin inhibits granulation so does it retard crystallization of stearine from refined cottonseed oil at lower temperatures²⁴. An analogous effect has been noted in the setting of cocoabutter at temperatures where some of the lower melting point fractions remain liquid²⁵. An effort was made to utilize the action of lecithin on surface tension to facilitate the pressing of oils, as with cocoabutter from chocolate liquor, but this has not yet proven significant²⁶.

Adding 0.5% to 2% of lecithin to shortening substantially increases the lubricating properties (shortening value) and emulsifiability^{27, 28}. Such a shortening would be intended for bakery use exclusively, in bread or cakes or biscuits and crackers. The lecithin causes the shortening to spread more readily throughout the dough and promotes uniformity and better moisture retention as well as increases tenderness. Instead of blending the lecithin directly with the shortening it may be first emulsified with water and then mixed with the fat but this should preferably be done shortly before use²⁹. In any event, to assure optimum results the bakery formula should be kept properly balanced.

Lecithin forms perfectly homogeneous milky emulsions with water which may be diluted almost indefinitely. One of the first uses for soya-lecithin was in oleomargarine where it replaced more expensive egg yolk added to improve the frying properties³⁰. Up to 0.30% of lecithin incorporated at any stage, usually in the churn, counteracts spattering and the sticking of milk solids in the frying pan and imparts desirable foaming and browning effects. At the same time there is some increase in spreadability and shortening value. Thus, with lecithin oleomargarine is a more universal household fat, for kitchen as well as table use. Butter, of course, contains a fractional percentage of lecithin derived from the milk^{31, 32}; favorable results have been reported with process or renovated butter. Oleomargarine and butter are emulsions containing much more fat than water. Several examples of the other type where water is the continuous phase may be given. In a 3% emulsion of oleo resin of capicum 0.50% of lecithin was satisfactorily used as the emulsifying

agent, while with a 50% castor oil or cod liver oil emulsion 4% to 5% of lecithin was used in a preparation stable for months.

Cake fillings and icings comprising shortening and water cream up to larger volume when lecithin is used. The moisture is more finely divided and uniformly distributed and the texture appreciably smoother³³. Likewise the surface of icings finishes with a more attractive lustre. "Lecithinated" fats for pan or slab greasing are more spreadable and go further.

Another instance of lecithin utility where fats must be emulsified in the presence of moisture may be seen in the manufacture of confectionery, especially chewing candies, such as caramels. Ordinarily the added fat floats on top during the cook and the candy itself tends to be greasy to the touch, the film of fat being readily oxidizable. A fractional percentage of lecithin causes the fat to disappear and mix throughout the batch during cooking and improves the handling and keeping properties of the caramel. Moreover, the caramel cuts better and cleaner due to the greater lubricating value of the fat³⁴. Lecithin can be used to similar advantage in boiled icings, such as butter-scotch.

Having an affinity for both oil and water and being adsorbed at interfaces, lecithin promotes the rapid and complete wetting by oils or fats of a wide variety of solid particles. This property, plus the fact that the oil will form a thinner continuous film, makes lecithin a time, labor and material saver. Thus, where plastic coconut butter or shortening is to be mixed with sugar to form a wafer filling, lecithin permits a higher solids content while maintaining the necessary workability; the mass has a better body and the fat is less likely to bleed from the sugar. So too in coatings where oil or fat is the liquid phase lecithin facilitates grinding and uniform dispersion and improves the flow and covering properties³⁵. The first 0.10% shows the greatest effect and with increasing additions the viscosity curve flattens out, depending on the physical properties of the solid and the proportion of free liquid. It may be noted that when mixed with oils as with water, lecithin gives a colloidal solution. However, while lecithin will form a stable emulsion or dispersion with water in any proportion, only relatively

small amounts can be dissolved in oils and fats. Its solubility is, of course, greater at high temperatures. The addition of lecithin does not reduce the viscosity of a fatty oil per se, the tendency is rather the reverse.

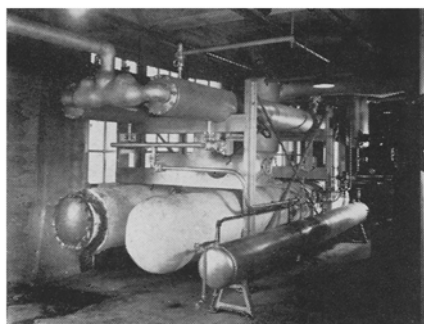
Lecithin finds many miscellaneous applications with oil and fat products. A small percentage incorporated in citrus oils and other oil soluble flavors acts as a fixative, reducing flavor losses due to volatilization, and at the same time assures better flavor distribution, particularly in the presence of moisture³⁶. Cosmetics, including shaving creams, made with lecithin possesses enhanced softening and penetrating value^{37, 38}. Liquid soaps so treated are milder and more thorough in cleansing action^{39, 40}. Peculiarly enough lecithin, which forms milky emulsions with water, gives a clear solution with liquid soap. Still other uses in conjunction with oily materials are in the drumming or fat liquoring of leathers⁴¹ and in the sizing of textile materials⁴². The addition of about 15% benzyl alcohol to the lecithin has been found helpful in making

water emulsions without undue stirring⁴³.

Hardly ten years have elapsed since lecithin became available commercially and was introduced to industry. In that period a variety of uses have been developed and factories built in the United States which are currently producing all that can be sold, with considerable capacity to spare. As consumption has mounted, the price trend has been downward to about $\frac{1}{3}$ of the 1929 level. This is simply an expression of the normal relationship between the cost of producing and selling as the numerator and the tonnage as the denominator. Many patents on methods of manufacture and use have encouraged missionary work in this field and made possible enlisting the interest and capital necessary for research and for plant equipment. The recovery of lecithin has increased the value of farm products and provided a new and useful material; its future depends more on expanding existing markets and discovering new uses than on solving manufacturing or technological problems.

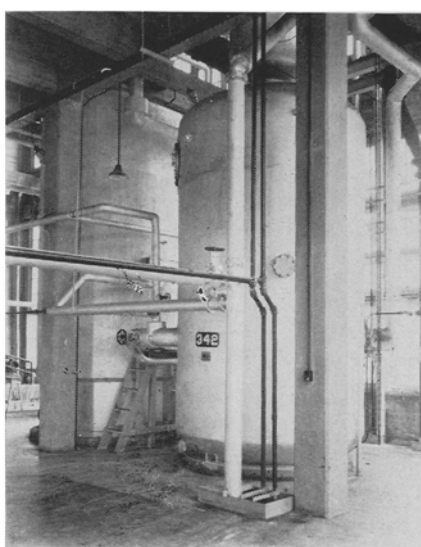
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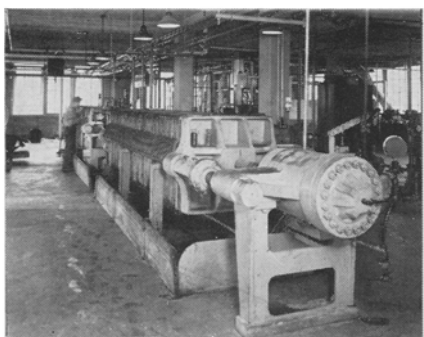


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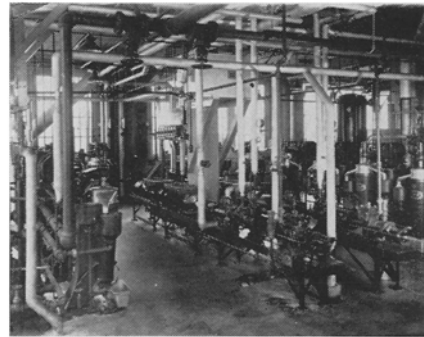
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