Phosphatides from Vegetable Oils

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PHOSPHATIDES are esters of a polyhydric alcohol, usually, but not necessarily glycerol, where the alcoholic groups have been esterified with long chain fatty acids and with phosphoric acid—organic base complexes. They can also be looked upon as triglycerides where one of the fatty acid molecules has been substituted by phosphoric acid combined with a nitrogen containing base. Lecithin, containing phosphoric acid-choline complex and cephalin, containing phosphoric acid-colamine complex are the two most important constituents of vegetable oil phosphatides.

The phosphatide content of vegetable oils varies generally from 0.1% to about 3%, though as high as 5% has been reported in mohua oil.[11] Like the triglycerides, they are found abundantly in ripe seeds.[3] The outside layers of these seeds contain a little more phosphatides than the central regions of the same seeds. During germination, the phosphatides accumulate in the germ. The phosphatide content has been found to vary roughly with the protein content of the seed rather than with its oil content. This is perhaps the reason why oils like that from coconuts having a low protein content are also low in their phosphatide content. On the other hand, soybean, cotton-seed and groundnut are higher in their protein content as also in their phosphatide content.

From the point of view of large scale recovery, only three oils need be considered. They are soybean, cotton-seed and groundnut. During the second world war, however, German oil mills could not procure imports of soybean and hence, rapeseed was mainly being handled. Although this contains comparatively little phosphatides, almost all German oil mills were equipped with plants for recovery of phosphatides from soybean as well as rapeseed, during and after the war.[22] Corn, sunflower and mohua oils have received considerable attention as sources but not on a very large scale. From the point of view of the Indian oilseeds processor, castor oil and mohua oil have been prominently recommended. The phosphatide content of some of these oils are as follows :—

Oil	% *Phosphatides*
Soybean[3]	2 – 2.5%
Mohua[11]	4 – 6.0%
Cotton-seed[3]	1 – 1.5%
Groundnut[3]	0.7%
Castor[4]	0.47%
Sunflower[3]	0.5%
Rapeseed[1]	0.1%

The methods for recovery of phosphatides are based on two main principles. Firstly, phosphatides contain a polar group and will therefore hydrate when brought into contact with water. Under this condition, they are no longer soluble in oil and hence separate out from the oil-phase. Secondly, although, like the triglycerides they are soluble in solvents like ethyl ether, petroleum, naphtha and hexane, unlike the triglycerides, they are insoluble in acetone. Hence, after hydration of the phosphatides, they can be separated at first by centrifuging and then by acetone extraction. There are mainly two reasons for the recovery of phosphatides during refining of oils. Technological opinion is agreed on the point that the presence of lecithin is one of the causes of the flavour reversion in soybean oil, a phenomenon whereby refined soybean oil gets back its flavour

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on storage. Hence, lecithin removal during refining is necessary.[21] Secondly, the scale on which lecithin is used in industry, makes any recovery desirable.

The first commercial method for the recovery of phosphatides from soybean oil was worked out by Bollmann about the year 1923 at the works of Hansa Muhle A. G. in Germany.[23] In the United States, commercial recovery was made possible by the year 1929.[8] It is of interest to note that about the same time, solvent extraction for oil seeds came to stay as a method of winning oil both in Germany as well as in the United States. This fact is important, since most of the methods for phosphatide recovery use solvent extraction as a first step.

In the Bollmann process, the oil from rapeseed or soybean is extracted with a suitable solvent in the extractor. The solvent is distilled from the miscella, the last traces being removed by countercurrent steam-stripping in a packed tower. The oil at the base of the tower, containing 0.5% moisture, is stirred in cylindrical mixing tanks with 2-3% water which is sprayed hot over the oil mass through perforated pipes arranged radially at the top of the tank. The operation is conducted at 60-70°C with violent agitation and the emulsion is immediately centrifuged. The resulting sludge is dried under vacuum. The product contains 60% phosphatides and 40% oil and in many cases is sold as such for use in margarine. But in some cases, the sludge is extracted with 4-5 volumes of acetone in a mixing pot, the insoluble material is allowed to separate and the supernatant layer is decanted. The operation is repeated four to five times in the case of soybean phosphatides and about ten times in the case of rapeseed phosphatides. In the final extraction, some acetone is left with the phosphatides and cocoa butter or a refined oil,equivalent to the crude oil originally present, is added. The acetone is then removed in a steam pan by distillation ; the purified lecithin is dried under vacuum. The lecithin obtained from rapeseed oil is reported to be inferior in quality to that obtained from soybean oil. The name lecithin, as used above, does not indicate the chemical compound of that name but implies a mixture of acetone insolubles which include lecithin, cephalin and phosphoinositides.

Thurman[19] advises the use of a precipitating agent containing moisture in small quantities for hydration purposes. Further, the use of a carrier liquid such as salt solution, which is heavier than the oil, while centrifuging, is claimed to lead to the discharge of gums without adherance to the bowl of the centrifuge. In another modification, he recommends the preprecipitation of gums other than phosphatides in a first stage by adding small quantities of an aqueous medium having a pH of approximately 7 to the oil. The precipitated material is separated and in a second stage, the residual oil is mixed with an aqueous medium having a pH between 2 and 6 to precipitate phosphatides which are less associated with impurities.[18] In a more recent patent, Thurman[17] has described a method by which phosphatides, sterols, carotenoids and tocopherols could be recovered from soybean, cotton-seed, groundnut or linseed oils. The precipitation of the gums is done by water or a weak solution of an electrolyte. The gums are dried in vacuum and then extracted with acetone. The extract contains oil, sterols, carotenoids and tocopherols which can be separated from each other by solvent extraction or molecular distillation. Acetone insoluble residue contains predominantly phosphatides. It is distilled in vacuum to remove acetone and is then extracted with hexane.

SET OF 5 HIGH ROLLS

(*Oils, Fats & Waxes Section*)

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The amount of water to be added and the temperature of hydration are very important factors. For this, the work of Helme and Desnuelle[5] on groundnut oil phosphatides is very useful. The following results are reproduced from their paper, in the table given below.

% H_2O added.	Emulsion weight in kg.	% Precipitated	% Loss of oil	Ratio *Lecithin/oil* in final product.
2	26	51	0·57	0·82
4	35	63	0·50	1·14
5	51	67	0·44	1·39
6	57	75	0·35	1·85
8	62	84	0·31	2·38
10	85	85	0·37	2·06
15	154	85	1·22	0·64

These workers started with solvent extracted groundnut oil obtained from groundnut cake. The oil contained 0.92% of lecithin. From the table, it is seen that at 8% water, 84% of phosphatides, as measured by their phosphorus content, are recovered. If the water is increased too much, increased amounts of emulsions are formed. Further, the loss of oil during washing is minimum at 0.31% and the final product has the highest lecithin content. The optimum pH was found to be 5, thus agreeing with Thurman's work. It was also found that up to 175°F, there was no substantial change in lecithin recovery. Above this temperature, a sharp reversion occurred. At 212°F only 20% of the phosphatides were recovered. Time of contact between water and oil was found to be optimum at 45 minutes. After hydration, the oil was centrifuged and the sludge separated was concentrated under vacuum by evaporating its moisture.

Molines and Desnuelle[10] have found out that greater the acid value of the crude oil from which phosphatides are to be recovered, larger the amount of water required to remove lecithin. Further, the phosphorus content of the technical lecithin recovered diminishes as the acidity of the oil increases.

In Julian and Engstrom's method for the recovery of phosphatides from soybean expeller "foots", the foots are dissolved in lecithin-free soybean oil and the phosphatides are emulsified with water containing a bleaching agent such as hydrogen peroxide in solution. The emulsion is separated from the bulk of the oil, dried and the crude phosphatides so produced are washed with a liquid such as acetone which will dissolve out the oil and the free fatty acids but not the phosphatides.

Lesyuis[9] has developed very recently a process for refining of sunflower oil and for simultaneous recovery of phosphatides for edible purposes. The process consists in filtering the hot oil at 60°C through a filter press and cooling to 16-18°C in a specially designed cylindrical cooler to precipitate the phosphatides. The mixture is refiltered through a filter paper in a filter press and then the filtrate is settled in settling tanks. The gelatinous precipitate from the filter paper and the sediment from settling tanks are pumped to a cylindrical vessel where they are diluted 1:1 with sunflower oil. The resulting mixture is steam heated to 105-110°C and then centrifuged for 30 minutes in a basket centrifuge. The precipitate containing 55-60% of the phosphatides, 1-2% moisture, 0.5% mucilagenous por-

tion is collected from the centrifuge and packed in parchment lined barrels or aluminium containers for shipment.

Chattarjee and Saxena[2] recommended the use of phosphatides obtained during solvent extraction of castor seeds as a substitute for egg lecithin. Their method lies in first extracting 99% of castor oil with denatured alcohol (containing 10% methyl alcohol) in a battery of four extractors. The alcohol is evaporated from the miscella and the oil filtered from the coagulated substances. The latter are further solvent extracted for phosphatide recovery. Gupta[4] extracted the above coagulated substances with benzene at room temperature. The first two extracts were discarded and subsequent extracts treated with acetone to yield a light tan precipitate of the phosphatide. The yield was 0.47% of the original oil. This source has been recommended for commercial recovery. Another possible source for commercial recovery in India would be mohua oilcake, which has been reported to contain about 6% of phosphatides. Saletore and Pandharipande[11] found that a 1:4 mixture of alcohol and benzene is the best solvent for phosphatide extraction from mohua cake.

A novel method for phosphatide recovery has been patented by Unschuld[20] and consists in passing a high voltage current of about 10,000 volts for a very short time (0.05 to 0.09 seconds) through the crude soybean oil previously heated to 160°C and then to subject the treated oil to a cold zone (0 to —54°C) at 28-29.5 mm. pressure when the phosphatides cleanly separate out. This method involves a more difficult and costly procedure and commercial recovery will be possible only where electricity is very cheap.

Where elaborate process like extraction with acetone followed by vacuum drying are not carried out, all the methods give commercial 'lecithin,' containing about 30% of free oil. The colour of the product obtained is brownish. Scholfield and Dutton[12] attribute the colour of soya lecithin to carotenoid and brown pigments. Where lighter grades of lecithin are required, bleaching has to be carried out. Bleaching by hydrogen peroxide has the greatest effect on carotenoids, little undesirable colour being left. The brownish colour of the phosphatides may also have been introduced due to an aldehyde-amine formed by heating of the oil during solvent stripping operation. To prevent any undue increase in colour, the drying of the gums should be done under vacuum for three hours at a temperature not exceeding 80-90°C. Other bleaching agents suggested include dibenzoyl peroxide, ammonium persulphate and sodium chlorite.

The free oil present in commercial lecithin acts as a carrier for the phosphatides and serves as a guard against deterioration at high temperatures. It also imparts a softness to lecithin and makes it suitable for use. The finishing stages of a process for manufacturing edible grades of lecithin consist in vacuum distilling the crude phosphatide emulsion to remove the odour and improve its taste, in extracting the phosphatides thereafter with acetone to separate oils and sterols and while still wet, in redissolving the acetone-extracted phosphatides in another refined oil such as cacao butter, coconut and groundnut oils to produce a phosphatide content of about 65%. The mixture is freed from residual acetone by agitation under vacuum.

Prior to the recovery of phosphatides from vegetable oils on a commercial scale as a by-product of the main oil processing industry, the principal use for phosphatides was in the pharma-

ceutical industry. For this, lecithin was being extracted from yolks of eggs. Naturally, the product was very costly. When, however, a commercial process for recovery from vegetable oils was perfected, its use was extended to many other fields and the price of lecithin progressively came down. For example, the price of lecithin in the U.S. in 1930 was the dollar equivalent of about Rs. 3/8/-. In 1950, American phosphatide producers manufactured about 400 short tons of lecithin. The price, however, had come down to Rs. 0-15-0 per lb. It is estimated that if the price of lecithin falls below about Rs. 0-8-0 per lb., it is not economical to recover lecithin.

Of late, the tendency has been to fractionate commercial lecithin on a large scale and to use the various constituents for more specific purposes—chemical, physical and biological. Scholfield and co-workers[14] have given the analysis of soya lecithin as 24% lecithin, 25% cephalin, 33% phosphoinositides and 7% carbohydrates. The method for their separation consists in first treating the commercial sample with acetone to free them from oil and then to treat the residue with 55% ethyl alcohol which dissolves free sugars present. The residue is re-extracted with acetone to remove the last acetone soluble portion and the low sugar content of phosphatides are extracted with absolute alcohol. The alcohol insoluble portion is separated by countercurrent distribution to give two portions containing phosphoinositides of differing partition coefficients. The alcohol soluble portion is rich in pure lecithin. Another technique which could be used for the fractionation of commercial lecithin is that of adsorption chromatography, by which choline containing phosphatides (like pure lecithin) are separated from choline-free phosphatides (like cephalin) by percolation through a column of magnesia or powdered cellulose.[3]

Industrial uses of lecithin: Mainly, three industries make use of 'lecithin' on a large scale. They are the Foodstuffs, Pharmaceutical and Soap and Fatty oil industries. Their use depends on three of their properties—surface activity, antioxidant nature and physiological properties.

Surface active properties: Bailey[1] classifies phosphatides in the category of naturally occurring surfactants. The hydrophobic group here consists of the fatty acid radical while the phosphoric acid-choline complex comprises the hydrophilic group. The use of lecithin as effective oil-soluble emulsifying and dispersing agents is hence explained. For example, lecithin is incorporated in margarine and chocolates as an emulsifying agent.[16] During the grinding of cacao, sugar, milk and other solids in a vehicle of cacao butter, lecithin spreads on the surface of the particles in a monomolecular layer, causing instant wetting, decreasing grinding time and producing a stable chocolate that does not change in viscosity on ageing, melting or agitation. Its emulsifying properties also enable it to be used in cometics, printing inks, petroleum products and in the fat liquoring process of leather manufacture. For use in oleomargarine, lecithin is dissolved in hydrogenated oil at 90-100°C and then centrifuged at 35-40°. The resulting product has a paste-like consistency and retains its stability for a year.

Antioxidant nature: Phosphatides by themselves are not antioxidants, as for example, when present alone in oils. However, when tocopherols or other antioxidants of the phenolic type are present, phosphatides are capable of increasing the antioxidant effects. In other words, phosphatides act as synergists. In commercial lecithin, this synergistic activity is confined only to the cephalin fraction and is attributed to the presence of a free hydroxyl group of phosphoric

acid. When it is incorporated in foodstuffs like biscuits, crackers or other baked goods, its synergistic activity is for the most part lost and only the surface active and nutritional properties remain.

However, both in liquid and solid soaps, lecithin imparts antioxidant properties. The stability of the lather is improved. Generally, about 2% lecithin is added after saponification. A German method[21] for the preparation of a lecithin soap consists in adding to a comparatively dry soap mass, prepared by rapid saponification method, a saturated stable lecithin compound such as lecithin formaldehyde or another lecithin ester combination in the form of a homogeneous emulsion. Lecithin is also added to refined oils to improve their stability to atmospheric oxidation. Lecithin with hydroquinone[6] has been found to be an effective antioxidant for vitamin A in halibut liver oil.

Another use of commercial lecithin which is, however, not based on its synergistic behaviour, but based rather on its chemical constitution, is in the oil industry as metal scavengers for removing metallic contaminants in oil which may be present due to contamination while in storage or by nickel during hydrogenation. The action is due to the phosphoric acid group which forms an inactive complex with iron, nickel and other heavy metals.

Nutritional and Pharmaceutical uses: In foods and pharmaceuticals, 'lecithin' introduces substances of high nutritional and medicinal value, such as choline and inositol, which have been classed with vitamins. Further, it also contains small quantities of tocopherols and biotin which have important physiological functions. It is also essential in the prevention of fatty degeneration of the liver. Lastly, lecithin ensures a better utilisation in the body for the fat soluble vitamins A and D.

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