

✂ The Industrial Uses of Special Lecithins: A Review¹

WILLEM VAN NIEUWENHUYZEN, Technical Manager, Lecithin Department, Unilever
Oil Milling Division, Unimills GmbH, Dammtorwall 15, 2000 Hamburg 36, West Germany

ABSTRACT

The surface activity and ultimately the performance of commercial lecithin can be improved by physical, chemical or enzymatic methods. These methods are reviewed along with a brief survey of the use of special lecithins in certain food and non-food applications. Emphasis is placed on margarine, instant foods, leather fatting and mosquito control systems.

INTRODUCTION

The world consumption of lecithins is estimated at 100,000 tons per year. In western Europe, 30,000 tons are used of which more than half is applied as modified lecithins. This shows the importance of developing lecithins with tailor-made performance, enabling the production of optimal end-products with the help of these additives.

In contrast to normal trade lecithin, which complies with regular trade specifications and is produced straight after the degumming process, special lecithins are defined as products which have been processed in such a way that a specific surface activity has been achieved.

Before describing the methods of modifying phospholipids, a survey of lecithin-application areas and the principle of surface activity will be given. Afterwards, the typical performance of modified lecithins in the food applications of margarine and instant products and in two new technical areas, leather fatting and mosquito control systems, will be presented.

Survey of Application Areas

Important food and non-food applications of lecithin are given in Tables I and II, respectively. The surface activity of the phospholipids contributes to various effects in the manufactured products, typical functions of which are described in the second section. The surface activity enables the use of lecithins as emulsifiers, wetting and dispersing agents. It would go beyond the scope of this survey to discuss all the effects.

Surface Activity of Phospholipids

Natural soya lecithin consists of a blend of phospholipids dissolved in oil. The formulas of the main phospholipids (Scheme I) indicate a balance between hydrophobic and hydrophilic parts in the molecules resulting in typical emulsifying properties.

Phosphatidylcholine (PC) has oil-in-water (O/W) emulsification promoting characteristics; phosphatidylethanolamine (PE) and to a lesser extent, phosphatidylinositol (PI), have water-in-oil (W/O) emulsifying properties.

In natural lecithin, the blend of the phospholipids gives a type of emulsifier with weak W/O and O/W emulsifying properties. For both types of emulsions, lecithin can be used, provided the other conditions such as pH, salt concentration and oil-water ratio are chosen carefully. Water hardness is also important since PE and phosphatidic acid (PA) can be flocculated by high concentrations of calcium and magnesium ions, and are therefore inactivated as emulsifiers.

This knowledge is applied in the production of lecithin additives with specific tailor-made properties.

MODIFICATION

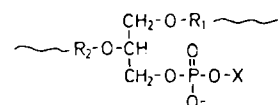
One principle of modifying lecithin as an emulsifying agent often consists of the removal or transformation of the PE fraction by which the calcium sensitivity is reduced and polarity becomes stronger. A second principle is the adaptation of the physical state by introducing the phospholipids

TABLE I
Important Food Applications for Lecithins

Application	Typical function
Bakery goods	Improvement of volume Fat dispersion Anti-staling
Chocolate	Reduction of viscosity Prevention of crystallization
Instant products	Wetting Dispersion
Margarine	Stabilization of product Prevention of spattering Browning and dispersion of the sediment

TABLE II
Non-Food Applications for Lecithins

Application	Typical function
Drugs	Biological emulsifier Choline supplier
Calf milk replacer	Fat emulsification Improvement of digestibility
Paints	Pigment dispersion Stabilization of emulsions
Leather fatting Mosquito control	Fat liquoring Reduction of surface tension



X = CH₂-CH₂-N⁺(CH₃)₃ phosphatidyl choline PC

X = CH₂-CH₂-NH₂ phosphatidyl ethanolamine PE

X =  phosphatidyl inositol PI

X = H phosphatidic acid PA

R₁, R₂ = fatty acid radicals

SCHEME I. Molecular structure of phospholipids.

into carriers such as oils, solvents, proteins or by deoiling the phospholipids. This is not only done for convenience in industrial use but also for a more effective performance.

Modification of phospholipids on an industrial scale is performed according to 3 principal methods: (a) by physical means, (b) by enzymes and (c) by chemicals.

MODIFICATION BY PHYSICAL MEANS

Alcohol Extraction

The principle of this process is based on the differences in the solubility of phospholipids in alcohols. Liquid-liquid extraction is used to obtain both alcohol-soluble PC-enriched fractions and alcohol-insoluble PE-enriched fractions. The multitude of parameters such as alcohol polarity, concentration, lecithin/alcohol ratio, temperature and extraction time permit the production of fractions with varying PC/PE ratios.

Starting with a PC/PE ratio of 1.2/1 in natural lecithin, by extraction with 90% ethanol, alcohol-soluble fractions with PC/PE ratio of up to 8/1 can be produced.

Acetone Extraction

As phospholipids are not soluble in acetone, this solvent is used for oil removal. Powdered and granulated phospholipid blends with 95-98% acetone insolubles are obtained.

Spray Drying with Proteins

Lecithins spray-dried onto proteins as a carrier have the advantage that powdered products are obtained at relative low cost. It is possible to obtain products with 30-50% lecithin. Using skimmed milk and whey, the lecithins are encapsulated by a film of casein, which contributes to good free flowing properties. However, it is possible to produce lecithin/vegetable protein blends with good free flowing properties, as well.

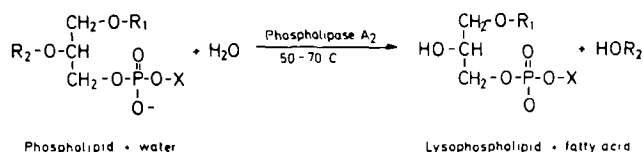
Spray Cooling with Synthetic Emulsifiers

Combinations of lecithins and, e.g., high melting mono- and diglycerides, can be effective emulsifiers. By spray cooling 30% lecithin and 70% mono- and diglycerides, flaked or powdered products can be obtained.

MODIFICATION BY ENZYMES

With the help of specific enzymes, partially hydrolyzed lecithins with pronounced O/W emulsifying behavior are produced.

Although, on a laboratory scale, several types of phospholipases are used, on an industrial scale, phospholipase A₂ is the most attractive. This enzyme specifically hydrolyzes the fatty acids at the β-position of the phospholipid molecules (Scheme II). By varying the temperature between 50-70 C, enzyme concentration and reaction time, partially hydrolyzed lecithins with enhanced surface activity are obtained. Each type of phospholipid has its own reaction speed under given conditions. These phenomena are also used to direct the production of a tailor-made product. By applying this enzyme on an industrial scale, a simulation of the reactions taking place in nature during the ripening of



SCHEME II. Lecithin hydrolysis with enzyme.

wheat and soybeans can be achieved.

MODIFICATION BY CHEMICALS

Hydrolysis by Acids and Alkali

Fatty acids are split off under acid and alkaline conditions. However, these processes are less specific than enzymatic hydrolysis. Lecithin with an undesirable dark color is often obtained.

Acetylation

Treatment with acetic anhydride acetylates the amino group of the PE. By varying conditions as temperature, reaction time and acetic anhydride concentration, the process can be performed with lecithin sludge and dried lecithin, achieving various degrees of acetylation. The principle of the process is the blocking of the "zwitterionic" group of the PE, thus improving the oil/water emulsifying properties.

Hydroxylation

High concentrations of hydrogen peroxides in combination with acids, especially lactic acid, cause the introduction of hydroxyl groups in the unsaturated fatty acid chain. In addition, the amino group of the PE is modified. The pronounced "hydrophilic" character enables the products to be dispersed easily in cold water.

APPLICATION

The great variety of modified lecithins offered to industrial customers contributes significantly toward solving technological problems in the processing of high-quality goods. This paper will be limited to discussing the use of special lecithins in 4 areas: margarine, instant foods, leather fatting and mosquito control systems.

Margarine

Margarine is a water/oil emulsion, in which up to 18% water of milk is homogenized as a dispersed phase in the continuous fat phase. The stabilization of the W/O emulsion is usually achieved by the addition of mono- and diglycerides. Mono- and diglycerides with saturated C16-C18 fatty acids are mostly used. In contrast to the function of mono- and diglyceride, the function of lecithins in margarine is to prevent spattering during frying.

For a long time, spattering has been explained as follows: when margarine is heated to over 100 C, the emulsion must be stable to prevent the water droplets from coalescing into big drops. Coalescence would cause an explosive evaporation accompanied by the spattering of hot fat.

Coalescence is prevented by lecithins, as the water droplets are surrounded by a film of phospholipids. During heating, the stabilized water droplets are transported smoothly to the surface, where a slow evaporation of the water takes place. A margarine with good frying properties produces a stable foam with no spattering.

This theory does not adequately explain the good anti-spattering properties of lecithins, because some coalescence of water droplets has been observed. During frying, a lecithin sludge is formed and one hypothesis could be that the lecithin particles in this sludge function as nuclei for the formation of small vapor bubbles.

In addition to its beneficial effect as an anti-spattering agent, lecithin in margarine also contributes to (a) fine dispersal of the protein sediment, (b) interaction with proteins to form a brown gravy and (c) intensification of taste (salt release).

Each type of margarine requires a specific lecithin quality. In high-salt margarine, the phospholipid composition of a high-quality natural lecithin acts as an effective anti-spattering agent. In low-salt and nonsalted margarines, however, the calcium and magnesium ions of the water and the milk proteins inactivate some phospholipids such as PE by flocculation. In these types of margarine, less calcium-sensitive lecithins are required. The solution has been found in the incorporation of fractions enriched in choline lecithin and partially enzymatic-hydrolyzed lecithin.

Instant Cocoa Drinks

Cocoa powder contains 10-25% cocoa butter, depending on the degree of deoiling. However, even cocoa powder with a low fat content still possesses a fat film on the surface or the cocoa particles. As a result, the dispersion in water of milk at temperatures below the melting point of the fat (35 C) is not possible.

In industry and in the home, it is most convenient if the cocoa powder has improved wetting behavior. By using agglomeration techniques, it is possible to produce instant cocoa products which can be dispersed easily at high and low temperatures.

In all types of agglomeration processes, lecithins must be applied in order to achieve products with optimal instant characteristics, remaining constant during storage of up to 9 months.

By spraying lecithins in the instantizing process, the hydrophobic part of the phospholipids is dissolved in the cocoa butter and the hydrophilic phospholipid chain is directed outwards. The affinity of these hydrophilic groups to water enables quick dispersion and wetting of the cocoa powder as it sinks into the substrate.

This property helps the instant performance to be maintained during storage. The phospholipids prevent fat exudation to the surface of the capillaries in the cocoa powder agglomerates, which would reduce the wetting properties. It is important to spray the lecithin finely and homogeneously on to the cocoa powder/sugar blends to obtain a thin lecithin layer and prevent the formation of lecithin clusters causing lumps.

In principle, the agglomeration process is performed in a fluid bed by means of a wet steam/air mixture. In the first stage, the introduction of the moisture causes the formation of agglomerates which are dried and separated in the second stage.

Depending on the design of the instantizer, various types of lecithin for the production of cocoa powders containing sugar are used: some techniques require the application of deoiled lecithin as a powder which is blown onto the other ingredients; other instantizers require the use of lecithin with 65% phospholipids. The lecithin is made into an emulsion with water and sprayed into the instantizer; a third category of agglomeration processes needs a very thin, fluid lecithin dispersed straight into the instantizer.

Besides the technological conditions and the physical state of the lecithins, the hydrophilic properties of the phospholipids are important. Apart from tailor-made lecithins based on natural phospholipids, other more hydrophilic products such as fractions enriched in choline lecithin or partially hydrolyzed lecithin contribute to

optimal instant properties.

These examples for instant cocoa drinks can be transferred with modifications to the processing of instant full-fat milk.

Leather

Although lecithin has sometimes been used as an emulsifier in the leather industry, its effective use in fat liquor is quite a new application.

The production of leather consists of a series of processes, from the salting of fresh skins to tanning to fatting. The tanning is performed with various vegetable, synthetic and mineral tanning agents. Afterwards, the tanned skin has to be greased to produce a supple leather, suitable for manufacturing goods. For many years, the fat liquors consisted of sperm whale oils. These oils are used as such and in combination with their sulfonated and sulfated derivatives. Because of shortage of these crude oils, substitutes have been found in, e.g., sulfonated products from other oils, including mineral oils.

The following properties are required of fatting agents: (a) deep penetration into the skin, (b) fixing in the leather, (c) good light fastness (resistance), and (d) low residual fat content in the used liquor.

It has been found that lecithin has a lubricating character. Natural lecithin, however, does not penetrate deeply into the skin because the phospholipids are structured in micelles. By improving the hydrophilic character of lecithins and preventing the formation of micelles in the emulsion, a good fatting result is obtained, resulting in leathers with firm grain, good tear and tensile strength and body.

Mosquito Control Systems

Mosquitos carry vector-borne diseases such as malaria in tropical countries. In other regions, mosquitos are also a nuisance. In the course of the years, mosquitos have become resistant to insecticides, causing increases in the mosquito populations. Physical and biological treatments thus are being investigated to control mosquito populations. One of the possibilities is a control system using lecithin. The principle of this system is the spraying of lecithin on the water to reduce the surface tension from 70 dyne/cm² to below 30 dyne/cm². This low surface tension permits a good spread of the lecithin film. Several investigators claim that the tracheae of the mosquito pupae cannot penetrate this film mechanically and the pupae are killed. However, it could be possible, as well, that phospholipids disturb the hydrophobic character in the inside of the breathing tracheae, causing water to enter. Trials in Kenya and Germany have shown that the method is effective and that natural enemies are not destroyed.

The advantages of lecithins are: (a) the films are stable, (b) the lecithins are biodegradable, and (c) the method can be applied in agricultural areas and drinking water reservoirs.

An effective application of these systems requires an extensive knowledge of the local ecology and environment.

[Received March 2, 1981]