

This invention relates to a synergistic antioxidant mixture intended to protect lipids against oxidation. The current trend in the field of antioxidants, particularly for use in foods, is to give preference to natural compounds showing antioxidant activity.

Esters of ascorbic acid with saturated fatty acids, particularly ascorbyl palmitate (AP) and ascorbyl stearate (AS), are known as antioxidants for lipids. This is also the case with tocopherols (TL) which have been found to show antioxidant activity in animal fats in which they are not naturally present. It is also known that a mixture of AP and TL is more active than each of these compounds on its own.

It has also been shown, for example by G. Pongraz in In.J.Vit.Nutr.Res. 43 (1973), that lecithin (LC), although not having any antioxidant activity of its own, greatly increases the activity of mixtures of AP and TL in butter oil and in sunflower seed oil.

This observation is confirmed in published Japanese patent application no. 80.069688 which relates to a mixture of AS, TL and LC in safflower oil and in lard.

In these known mixtures, the ascorbic acid (AA) is not used as such, but in ester form (AP, AS) for the simple reason that it is not liposoluble. According to G. Pongraz in the Article cited above, AP and AS are equivalent from the point of view of their antioxidant activity in lipids, preference being attributed to AP by virtue of its slightly better liposolubility.

US-A-2,432,698 relates to the protection against oxidation of liposoluble vitamins A and D particularly sensitive to oxidation in the form of a concentrated dispersion in a solid support or of a fish liver oil containing these liposoluble vitamins.

The antioxidant mixture used contains as essential constituents:

- niacin or one of its derivatives and
- a vegetable material containing natural antioxidants in the form of a flour of seeds, kernels or pulses or extracts, concentrates or fractions of such materials.

5 In cases where a fat is to be protected, it is pointed out that a mutual solvent for the water-soluble antioxidant compounds (in this case niacin amide) and the liposoluble antioxidant compounds of the mixture has to be added for incorporation in the fat although this solvent is not
10 subsequently eliminated. It is for this reason that preference is given to the liposoluble solvents in this case.

It has now surprisingly been found that, when used in the presence of TL and LC, AA shows far better antioxidant
15 activity than its esters in anhydrous systems, particularly lipids.

Thus, the synergistic antioxidant mixture according to the invention is characterized in that it comprises toco-
20 pherol, ascorbic acid and a phospholipid in quantities of 2.5 to 10% tocopherol and 2.5 to 20% ascorbic acid, based on the weight of the phospholipid, and in that it forms a stable dispersion of ascorbic acid in an anhydrous lipophilic medium.

The tocopherol used may be α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol or mixtures thereof, for example
25 a natural mixture emanating from a vegetable oil, for example soybean oil, wheatgerm oil, cottonseed oil.

The phospholipids used may be of animal or vegetable origin, milk, egg, soya. They are preferably lecithins,
30 for example commercial lecithins, purified lecithins, soya lecithin fractions. The phospholipid provides for the formation of a a stable dispersion of the AA in an anhydrous product, for example a fat or a food containing a fat or even a cosmetic product containing a fat. It is
35 preferred to use soya lecithins or fractions thereof which

are abundantly available and economical.

The antioxidant mixture according to the invention advantageously contains 5% TL and 5 to 20% AA, based on the weight of the phospholipid.

5 The present invention also relates to a process for the production of the antioxidant mixture according to the invention, characterized in that the phospholipid and the tocopherol are mixed with stirring at a temperature of or below 60°C, ascorbic acid dissolved in a polar solvent is
10 progressively added to this premix in the presence of an inert gas and the solvent is removed at a temperature of or below 60°C.

 In one advantageous embodiment of the process according to the invention, the mixture is prepared by combining
15 LC and TC with stirring at a temperature of or below 60°C while an inert gas, for example nitrogen, is passed through. AA dissolved in a low-boiling polar solvent, for example ethanol, is then gradually added to the resulting premix, after which the solvent is removed at a temperature
20 of $\leq 60^\circ\text{C}$ in a light vacuum. The mixture obtained is a clear, viscous liquid which may be used in different ways, for example by incorporation with vigorous stirring in a fat to be protected, preferably with heating, the mixture being at a temperature of around 60°C.

25 The present invention also relates to a process for the protection of a fat or a fat-containing food or cosmetic product against oxidation, characterized in that the antioxidant mixture according to the invention is incorporated in the fat or in the food or cosmetic product in a
30 quantity of 0.55 to 2.3%, based on the weight of the fat.

 If less than 0.55% by weight is used, there is a danger that the desired synergistic effect might not be obtained on account of the inadequate quantity of phospholipid or antioxidant. If more than 2.3% by weight is used,
35 there is a danger that unwanted secondary effects, such as

for example variations in taste or odour or foaming, might occur.

Finally, the present invention relates to a process for the protection of a fat against oxidation by incorporation of ascorbic acid, phospholipid and tocopherol, characterized in that the phospholipid is added to the fat, the tocopherol and the ascorbic acid are dissolved in a polar solvent, the ascorbic acid solution and tocopherol are mixed with the fat containing the phospholipid, the solvent is removed at a temperature of or below 60°C in the presence of an inert gas so that the tocopherol represents 2.5 to 10% by weight of the phospholipid and the ascorbic acid 2.5 to 20% by weight of the phospholipid and in that the tocopherol, the ascorbic acid and the phospholipid represent 0.55 to 2.3% by weight of the fat.

The polar solvent used is preferably ethyl alcohol.

The fats to be protected in accordance with the invention are preferably those which are most vulnerable to oxidation, for example those which are rich in unsaturated fatty acids, particularly polyunsaturated fatty acids. Fats such as these include vegetable oils, for example wheatgerm oil, grapeseed oil, corn oil, soybean oil, safflower oil, olive oil, evening primrose oil, borage oil, particularly black currant seed oil. Examples of animal fats vulnerable to oxidation are chicken fat, butter oil, oils of marine animals, particularly fish.

The foods and cosmetic products to be protected are preferably those which contain fats such as these.

The invention is illustrated by the following Examples in which the percentages and parts are by weight unless otherwise indicated.

Examples 1 to 6

The antioxidant power of the mixtures according to the

invention in the protection of fish oil against oxidation is evaluated by the Fira.Astell® accelerated oxidation test.

Preparation of the samples:

5 Samples of 4 g stabilized oil are prepared as follows:
The antioxidants are dissolved in absolute ethanol in a
quantity of 125 mg/25 ml and the solution is mixed with the
oil to which the lecithin has optionally been added. The
ethanol is used in a quantity of 0.5 to 1.5 ml, depending
10 on the concentrations used. The ethanol is then eliminated
by evaporation at 60°C for 2 hours while the sample is
purged with nitrogen.

Oxidation test:

15 The sample is placed in a hermetically sealed glass
reactor provided with a magnetic stirrer. The reactor
itself is placed in an oil bath at the selected temper-
ature. The atmosphere in the reactor is air. The head
space communicates by a flexible tube with a differential
20 manometer connected to a recorder. When oxidation is in
progress, the quantity of oxygen absorbed is indicated by
the pressure difference observed. The induction time is
graphically determined from the transcribed pressure curve
as a function of time by intersection of the tangent to the
25 curve with the time axis.

The results obtained are shown in Table I below, in
which the induction times obtained without additive (C0),
by the various additives on their own (C1 to C3) or in
pairs (C4 to C13) are shown by way of comparison.

Table I

5	Examples	Antioxidant additive, based on oil			Induction time ¹ (h) at		
		TL (ppm)	AA(ppm)	LC(%)	60°C	80°C	100°C
10	1	250	250	1	-	2.7	-
	2	250	500	1	-	9.1	-
	3	500	500	1	-	12.8	3
	4	500	1000	1	-	23.2	5.2
	5	1000	500	1	-	11.2	-
	6	500	2000	1	-	18	-
15	Comparisons:						
20	C0	-	-	-	7	0.5	0.1
	C1	500	-	-	12	-	-
	C2	-	1000	-	11.5	-	-
	C3	-	-	1	10	1.6	-
	C4	500	250	-	11.7	-	-
	C5	500	500	-	17	2.9	-
25	C6	250	500	-	-	2.5	-
	C7	250	1000	-	-	2.9	-
	C8	500	1000	-	-	2.5	-
	C9	1000	500	-	-	3.6	-
30	C10	2000	2000	-	-	2.7	-
	C11	500	-	1	-	-	2.2
	C12	1000	-	1	-	1.2	-
	C13	-	500	1	-	-	1.1

Legend:

ppm = parts per million

LC = purified soya lecithin (Topcithin®).

5 ¹ The results obtained for the induction time at the various temperatures indicated may be compared by using an approximate factor of 4 for the values at 100°C in relation to the values at 80°C.

10 Table I above shows that the addition of the ternary mixture TL, AA and LC has an effect such that the fish oil remains stable approximately 5 to 26 times longer than the additive-free oil (1 and 4 compared with C0) and approximately 12 times longer than the oil containing one or other of the antioxidants in comparable quantities (4 compared with C1-C3).

15 The antioxidant effect of the ternary mixture is also higher by a factor of approximately 3 to 9 than that of the binary mixtures (2 to 5 compared with C5, C6, C8 and C9).

20 Accordingly, the various additives have a synergistic effect.

Example 7

25 The induction times of fish oil containing the ternary mixtures of Examples 3 and 4 are compared with those obtained for ascorbyl palmitate (AP) on its own or in the form of binary or ternary mixtures with TL and LC using the Fira.Astell® oxidation test described above.

The results are shown in Table II below.

Table II

5	Comparison	Antioxidant additive			Induction time (h) at		
		TL(ppm)	LC(%)	AA ¹ (ppm)	60°C	80°C	100°C
10	C14	-	-	500	8.1	1.8	-
	C15	-	1	500	-	-	0.2
	C16	-	1	1000	-	-	1.3
	C17	500	1	500	-	4.1	1
	C18	500	1	1000	-	8.1	2.2
15	According to Example 3				-	12.8	3
	According to Example 4				-	23.2	5.2

Legend:

¹ The content indicated is based on ascorbic acid in the form of ascorbyl palmitate.

LC = Topcithin®

Comparison of the induction times of the ternary systems C17 and Example 3 and C18 and Example 4, respectively, shows that the antioxidant effect is increased by a factor of 2.3 to 3.1 by replacement of the ascorbyl palmitate by ascorbic acid. This is all the more unexpected as ascorbic acid is completely insoluble in the oils.

Examples 8 to 12

The induction times at 100°C of fish oil stabilized by antioxidant mixtures containing 500 ppm TL, 1000 ppm AA and 1% of various lecithins are determined by the Fira.Astell® oxidation test described above. The results are shown in Table III below:

Table III

Example	Emulsifier	Induction time (h)
5	8	Azol [®] : soya lecithin fraction mixed with approximately 60% triglycerides
10	9	Centrophase [®] : a mixture of substantially equal quantities of soya lecithin and triglycerides
15	10	M-C-Thin [®] : a mixture of soya phospholipids: phosphatidyl choline, phosphatidyl ethanolamine, meso-inositol phosphatide
20	11	Métharin [®] : a mixture of soya phospholipids and mono-, di- and triglycerides
25	12	Topcithin [®] : refined soya lecithin poor in heavy metals

Example 13

The induction times of chicken fat stabilized with the antioxidant additives is determined using the Rancimat[®] accelerated oxidation test.

The Rancimat test differs from the Fira.Astell[®] test in the fact that air is passed through a test tube containing a 5 g sample of fat at 100°C and the conductivity of the volatile secondary products formed during oxidation and

entrained with the stream of air is measured. The induction time is graphically determined from the recorded conductivity curve as a function of time by intersection of the tangent to the curve with the time axis.

5 The results are shown in Table IV below:

Table IV

		Antioxidant additive			Induction time (h)
		TL(ppm)	AA(ppm)	LC(%)	
10		100	500	1	47.9
15	Comparison	1000	-	-	13
	Comparison	-	500	-	7.4
	Without additive				5

20

Legend:

LC = Topcithin®

25 The surprising antioxidant effect of the ternary mixture is confirmed in chicken fat.

Example 14

30 The induction times at 100°C of corn oil stabilized with various antioxidant additives is determined using the Rancimat® oxidation test described above. Corn oil already naturally contains approximately 310 ppm δ-tocopherol (TL).

The results are shown in Table V below:

Table V

	Antioxidant additive		Induction time (h)
	AA(ppm)	LC(%)	
5			
	250	0.5	34.6
	Comparison	250	20.8
10	With no antioxidant other than the TL naturally present		10

Legend:

15 LC = Topcithin®

20 It can be seen that the surprising antioxidant effect of the ternary mixture is confirmed in the case of corn oil where one of the antioxidants of the mixture, namely tocopherol, is already naturally present.

Examples 15 to 17**(Example 15)**

25 1000 g LC (Topcithin®) and 60 g TL are heated to 60°C while nitrogen is bubbled through. 100 g AA dissolved in 2.5 l absolute ethanol are then progressively added thereto with mechanical stirring over a period of 5 h. The ethanol is then evaporated at 60°C under a light vacuum until the mixture is constant in weight. On completion of the operation, the mixture becomes completely transparent.

30 99 kg black currant seed oil are heated under nitrogen to 90°C in a closed double-jacketed tank. The above antioxidant mixture heated to 60°C is then added with vigorous stirring, after which the stabilized oil is cooled to ambient temperature over a period of 20 minutes.

(Examples 15 to 17)

The induction times at 100°C of the oil stabilized with different quantities of antioxidant additives and without additive is determined by the Fira.Astell® oxidation test described above.

The results are shown in Table VI below:

Table VI

10	Example	Antioxidant additive			Induction time (h)
		LC(%)	TL(ppm)	AA(ppm)	
	15	1	600	1000	23
15	16	0.5	250	500	14.2
	17	2	1000	2000	30
	Comparison		no additive		3.5

The non-stabilized black currant seed oil has an induction time approximately 4 to 9 times shorter than those obtained by addition of the antioxidant mixtures LC, TL and AA.

CLAIMS

1. A synergistic antioxidant mixture, characterized in that it comprises tocopherol, ascorbic acid and a phospholipid in quantities of 2.5 to 10% tocopherol and 2.5 to 20% ascorbic acid, based on the weight of the phospholipid, and in that it forms a stable dispersion of ascorbic acid in an anhydrous lipophilic medium.
2. A mixture as claimed in claim 1, characterized in that it contains about 10% tocopherol and from 5 to 20% ascorbic acid, based on the weight of phospholipid.
3. A mixture as claimed in claim 1 or 2, characterized in that the phospholipid is soya lecithin, egg yolk lecithin or fractions thereof.
4. A process for the protection of a fat or a fat-containing food or cosmetic product against oxidation, characterized in that 0.55 to 2.3% of the mixture claimed in claim 1, based on the weight of the fat, is incorporated in the fat or in the food or cosmetic product.
5. A process for the production of the antioxidant mixture claimed in claim 1, characterized in that the phospholipid and the tocopherol are mixed with stirring at a temperature of or below 60°C, ascorbic acid dissolved in a polar solvent is progressively added to this premix in the presence of an inert gas and the solvent is removed at a temperature of or below 60°C.
6. A process for the protection of a fat against oxidation by incorporation of ascorbic acid, phospholipid and tocopherol, characterized in that the phospholipid is added to the fat, the tocopherol and the ascorbic acid are dissolved in a polar solvent, the ascorbic acid solution and tocopherol are mixed with the fat containing the phospholipid, the solvent is removed at a temperature of or below 60°C in the presence of an inert gas so that the tocopherol represents 2.5 to 10% by weight of the phospholipid and the ascorbic acid 2.5 to 20% by weight of the



phospholipid and in that the tocopherol, the ascorbic acid and the phospholipid represent 0.55 to 2.3% by weight of the fat.

5 7. A fat or fat-containing food or cosmetic product protected against oxidation by the process claimed in claim 4 or 6.

8. An animal fat, more particularly oil of marine animals, protected against oxidation by the process claimed in claim 4 or 6.

10 9. A vegetable oil, particularly black currant seed oil, protected against oxidation by the process claimed in claim 4 or 6.

