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REVIEW

Photo-oxidation and photoprotection of foods, with particular reference to dairy products An update of a review article (1993-2000)

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RÉSUMÉ

Photo-oxydation et photoprotection des denrées alimentaires, en particulier des produits laitiers. Mise à jour d'un article de synthèse (1993-2000).

Le présent travail actualise un article de synthèse paru en 1993 sur ce sujet. Il synthétise les principales nouvelles données et connaissances acquises à ce jour, notamment dans le domaine de nouveaux matériaux d'emballage attractifs et prometteurs comme le polyéthylène téréphtalate (PET). Après un bref rappel théorique des mécanismes qui expliquent la photo-oxydation des produits alimentaires, notamment les effets conjugués (synergie) de la lumière et de l'oxygène ainsi que le rôle clé joué par la riboflavine comme sensibilisateur, il passe ensuite en revue les principaux effets de la photo-oxydation sur les produits laitiers : perte de vitamines, oxydation des lipides insaturés, décoloration et apparition de défauts de la flaveur. Dans sa conclusion, ce travail propose un certain nombre de mesures simples et concrètes permettant de limiter, voire de prévenir ce type de réaction quant aux choix i) de la lumière/de l'illuminant utilisé(e), ii) de la translucidité et de la perméabilité de l'emballage à l'oxygène et iii) des conditions de stockage.

Mots clés : *photo-oxydation, photodégradation, photosensitivité, produit laitier, emballage.*

SUMMARY

This paper updates a previous review published in 1993. It surveys new data and recently published findings, e.g. promising modern packaging materials such as polyethylene terephthalate (PET) which are attractive to the consumer. After a brief theoretical outline of the mechanisms of the photo-oxidation of foodstuffs, in particular the combined effects (synergy) of light and oxygen, and the key role played by riboflavin as a sensitiser, the review surveys the principal effects of photo-oxidation on dairy products: loss of vitamins, oxidation of unsaturated lipids, discolouration and formation of off-flavour. In the conclusion, this paper proposes a number of simple and concrete measures for limi-

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ting or even preventing these reactions by choosing i) the light source, ii) the transmittance and oxygen permeability of packaging materials and iii) the storage conditions.

Key-word: *photo-oxidation, photodegradation, photosensitivity, dairy product, packaging.*

1 – INTRODUCTION

Ultraviolet, visible and infrared light are located in one of the most-studied regions of the broad spectrum of electromagnetic waves. They are energy sources, which are often highly valuable and useful (daily life, vision, photosynthesis, photovoltaic energy, heat production, etc.) but sometimes also undesirable and damaging (e.g. discolouration of pigments, ageing of materials, induced off-flavour, etc.). The latter situation is encountered with food, especially with white wine, beer, and with dairy products which are well known for being extremely sensitive to light. Indeed, dairy products do contain a high amount of riboflavin (vitamin B_2), a strong photosensitiser able to absorb energy and, by activating oxygen molecules, to be shifted to higher energy levels (excited states). These may in turn induce a cascade of oxidation reactions, generally (auto)catalytic, leading finally to great losses of valuable nutriments such as vitamins and amino acids, to discolouration of foods as well as to formation of strong off-flavours such as aldehydes, ketones, methional and dimethyldisulfide.

The prevailing occurrence of light induced off-flavour (taste and odour) in pasteurised milk was recently demonstrated in an investigation carried out by the Hygiene Institute in Hamburg (TARNOWSKI and FRESE, 2000). Approximately 82% of all these pasteurised milks (with a 4% fat content), two thirds of which were supplied in colourless glass bottles, were the subject of complaints about such off-flavour.

A broad review was published on this topic (BOSSET *et al.*, 1993a) several years ago as well as another review on photodegradation of foods (SPIKES, 1981). Another review article is currently being prepared (MORTENSEN *et al.*, 2002). Further data have since been published on this subject and the trend is clearly towards more active and specialised packaging materials (POLDERVAART, 1999). In this frame, marketers unfortunately seem to neglect this key role of the packaging material, and often favour the direct (colourless) view of the content of the package which they want to appear whiter, and consequently more "natural". For instance, red-brown pigmented glass jars, which were judged to be the best in a comparison of various packaging materials used for plain yoghurt (BOSSET *et al.*, 1993b) were abandoned due to marketing decision in favour of colourless polyethylene jars judged to be the poorest in the same series (Anonymous, 1999a, 2000; RESL, 2000). Recent laws, where the polluter must pay, have led to drastic reductions in packaging to save recycling costs. Some new packaging materials have such a high light transmission that reduction in vitamin content and quality of the food may occur due to the presence of oxygen and natural photosensitiser (ZIEGLEDER, 1995). The correct choice of packaging material for milk and dairy products should lead to an increase in the shelf life of the products without any expensive addition and/or special treatment (DEMAN, 1978). The aim of the current paper is to update our review (BOSSET *et al.*, 1993a) as exhaustively as possible, and to include some recent information on new materials and their potential for protection against light.

2 – CHARACTERISTICS OF LIGHT AND GENERAL VIEW OF LIGHT-INDUCED FOOD DEGRADATION

Visible light covers the wavelength range from 380 to 780 nm. The Ultraviolet (UV) range, with more energetic radiation, is at shorter wavelengths, and the Infrared (IR) range at longer wavelengths. The UV range itself can be divided into UV A (380-320 nm) and UV B (320-280 nm). The emission spectrum of natural sunlight covers the whole range from 300 up to 800 nm (see *figure 2* in BOSSET *et al.*, 1993a). *Table 1* summarises the wavelength ranges corresponding to the various emitted and absorbed (complementary) colours of visible light.

Table 1

Wavelength of colours of visible light

Wavelength region (nm)	Perceived colour	Absorbed (complementary) colour
380-440	Violet	Yellow-green
440-480	Blue	Yellow
480-490	Green-blue	Orange
490-500	Blue-green	Red
500-560	Green	Purple
560-580	Yellow-green	Violet
580-600	Yellow	Blue
600-620	Orange	Green-blue
620-750	Red	Blue-green

Both visible and UV ranges can lead to the degradation of food (BOSSET *et al.*, 1993a; ROSENTHAL, 1992). In general, the light absorbed by one or several of food components is subsequently able to produce some photochemical reactions. The resulting reduction in the quality of milk and dairy products is particularly well highlighted by the loss of riboflavin (vitamin B_2) and by lipid oxidation. Both are induced by the photosensitization of riboflavin itself (LENNERSTEN, 1995).

Light has a direct effect on the molecules that absorb it. These molecules are first excited and then lead to a cascade of photochemical reactions, which may be direct (isomerisation, rearrangement, dissociation) or indirect by energy transfer to other molecules, particularly oxygen (SKIBSTED, 2000). In food, most lipid, protein and sugar fractions do not themselves absorb light in the visible region of the spectrum, but are sensitive to the excited forms of oxygen. Some molecules absorbing into the visible range, e.g. vitamin B_2 (riboflavin) in milk, act as photosensitiser by transferring the energy absorbed from light into highly reactive forms of oxygen. The ability of riboflavin to generate singlet oxygen in milk after exposure to visible light has been confirmed by measurement of a stable radical (2,2,6,6-tetramethyl-4-piperidone-*N*-oxyl) by electron spin resonance (ESR) spectroscopy (BERLINER and OGATA, 1997; BRADLEY and MIN, 1992). After photodegradation riboflavin breaks down to lumichrome and probably formylmethylflavin. The former is itself a strong photosensitiser, but has not been so far exhaustively investigated (PARKS and ALLEN, 1977).

Other photosensitisers, such as chlorophyll and tetrapyrrole derivatives (porphyrin), produce singlet oxygen very quickly (BOCK and HARNETT, 1989; KESSEL *et al.*, 1993) when they are extracted or removed from the native state inside membrane proteins. Therefore, foods containing pigments such as porphyrin (meat products) or chlorophyll derivatives (vegetables) are also potential producers of singlet oxygen and sensitive to photodegradation. This is confirmed by the photosensitization of foods containing chlorophyll derivatives, which absorb in the red part of the spectrum (620-700 nm) (RIEBLINGER and ZIEGLEDER, 1998). Complete protection against visible light is therefore advisable due to the absorption capacity in the blue-green by riboflavin in milk and dairy products as well as in the red part of the spectrum by foods containing chlorophylls or porphyrins.

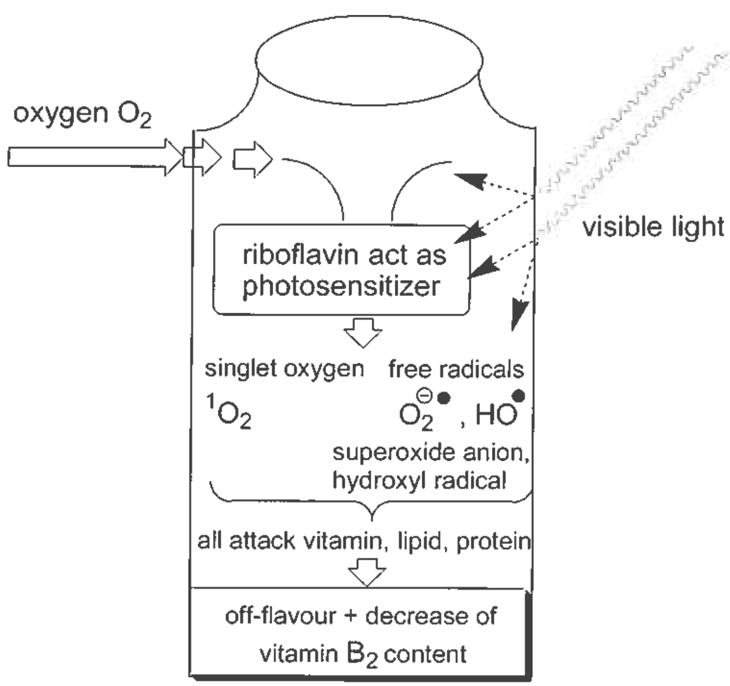

Figure 1

Light-induced effects onto milk and dairy products

Singlet oxygen and free radicals such as superoxide O_2^-, then diffuse into the medium and react with surrounding compounds contained in the food. This process is responsible for the extensive degradation of lipid, protein and sugar even without any direct interaction with light. Therefore the presence of a photosensitiser even at a ppm (mg/kg) level (MUNOZ *et al.*, 1994) may be responsible for the continuous and *in situ* production of a highly reactive form of oxygen. The key roles of the packaging material are protection against both oxygen and light (Anonymous, 1999b) (*figure 1*), the factors acting together as summarised in *figure 2*.

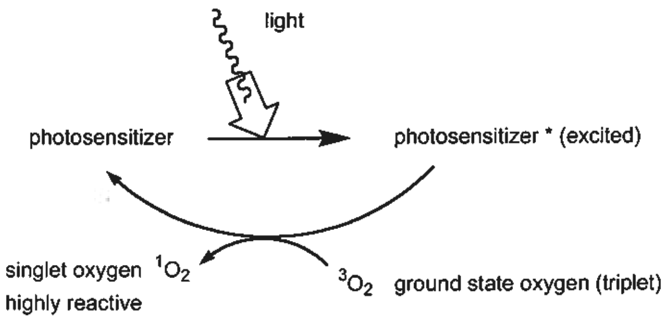

Figure 2

Synergy of light and oxygen effects

3 – PHOTOSENSITIZED CHEMICAL REACTIONS IN MILK PRODUCTS: THE KEY ROLE OF RIBOFLAVIN

Recently SKIBSTED (2000) reviewed the light-induced changes in dairy products exposed to visible light and pointed out that all the observed phenomena can be related to the following two types of chemical reactions:

A) The reactions of singlet oxygen with protein, lipid and vitamins give rise to the formation of oxidation products, some with unpleasant off-flavours (e.g. "burnt feather"), and to the destruction of riboflavin.

B) The reactions of free radicals (O_2^-, $HOO^\bullet$, $HO^\bullet$) induce a cascade of reactions leading to oxidation products, often themselves unstable, which are responsible for the deterioration of food (e.g. "cardboard like" flavour).

A precise distinction between these two types of reaction is sometimes difficult due to the similarity of the unstable intermediate reaction products such as the hydroperoxide and the hydroxyl radical $HO^\bullet$ which can result from both mechanisms. This fact can explain the differing interpretation of results (BEKBÖLET, 1990) in the literature, especially in quenching experiments. It has been shown in several reports that the effect of light on milk and other food products is related to the simultaneous presence of oxygen as substrate and of naturally occurring molecules acting as photosensitiser (BOSSET *et al.*, 1993a; SANDMEIER, 1996). In dairy products, the main photosensitiser is riboflavin (BRADLEY and MIN, 1992; SKIBSTED, 2000), an orange-yellow, highly light sensi-

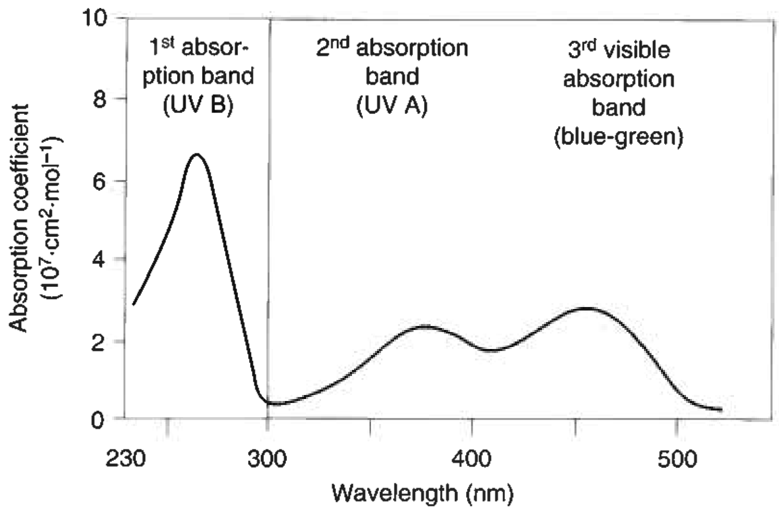

Figure 3
Absorption spectrum of riboflavin

tive vitamin (FOX and THAYER, 1998; TOYOSAKI and HAYASHI, 1993). Its three absorption bands are shown in *figure 3*. The third band (shadowed zone) in the visible region (blue to green, broad maximum at 430-460 nm) is the main band responsible for the photo-oxidation of food, especially of milk and dairy products. The photochemical reactions and energy exchange in the presence of riboflavin are summarised in *figure 4*.

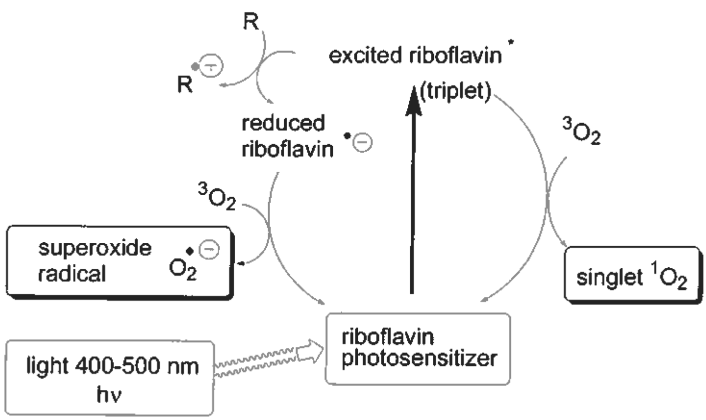

Figure 4
Photochemical reactions and energy exchange in the presence of riboflavin, where R represents any substrate (carbohydrate, amino acid) susceptible to be oxidised by riboflavin and this independently of the presence of oxygen

Acting as a photosensitiser, riboflavin transfers light energy to other molecules such as the oxygen dissolved in the milk. As a recipient of energy from the photosensitiser, oxygen in its ground state (triplet state for the O_2 molecule written $^3O_2$) is then excited to singlet oxygen ($^1O_2$), a highly reactive chemical species (photochemical reaction of type II). In turn, the riboflavin can be transformed into a reduced form, by oxidation of substrate, and can react with $^3O_2$ to form the anion radical superoxide O_2^{-} (reaction of type I). The electrophilic character of singlet oxygen explains typical addition reactions with all electron rich chemical species with a polar bond such as unsaturated lipids, riboflavin (TOYOSAKI and HAYASHI, 1993), vitamin D (LI and MIN, 1998), thiamine (vitamin B_1), pyridoxal (derivative of vitamin B_6), ascorbic acid (KIM *et al.*, 1993), glucose (SILVA *et al.*, 1999), folic acid, as well as with sulphur containing compounds such as methionine. The riboflavin-sensitised photo-oxidation of ascorbic acid can be affected by some amino acids (JUNG *et al.*, 1995), in particular tryptophan (SILVA, 1992) and tyrosine (SILVA and GODOY, 1994). More generally, the reaction of singlet oxygen with sulphur containing proteins and amino acids is able to produce sulphur containing volatile compounds such as dimethyldisulfide (DIMICK, 1982; DIMICK and KILARA, 1983). This compound, characterised by GC-MS and olfactometry, was claimed to be the agent responsible for the off-flavour of light exposed milk (JUNG *et al.*, 1998a). Some typical reactions of singlet oxygen are summarised in *figure 5*.

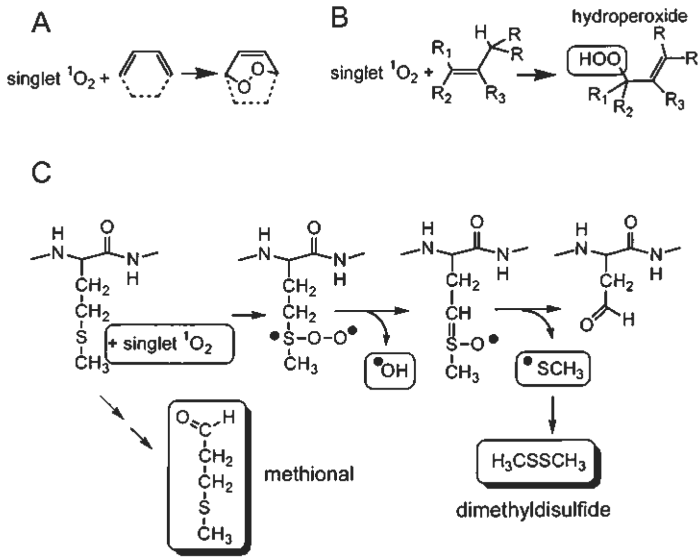

Figure 5

Reaction of singlet oxygen with an aromatic cycle (**A**), a double bond (**B**) or a sulphur compound (**C**)

The singlet state of oxygen is only 92 kJ/mol higher than the ground state. Therefore the energy of any region in the visible spectrum is sufficient to produce singlet oxygen in the presence of a photosensitiser. It absorbs everywhere in the visible spectrum and has a triplet state at about 104 kJ/mol higher than its ground state. In comparison the energy of a photon at 800 nm is 149 kJ/mol.

The correlation between the duration of exposure of the food to light, the presence of riboflavin and the resulting off-flavour has already been demonstrated (SATTAR and DEMAN, 1975) but recent studies deal in more detail with the relationship between the kinetics of headspace oxygen uptake, light intensity, occurrence of oxidation products and riboflavin content in food and model systems.

4 – EFFECTS OF PHOTO-OXIDATION ON MILK AND DAIRY PRODUCTS

4.1 Vitamins and off-flavour

An overview on the influence of light on water-soluble vitamins in milk was recently published (SHARMA and LAL, 1998). The exposure of dairy products to natural or artificial light is responsible for a large decrease in the contents in vitamins C and B_2. The loss of riboflavin is highly correlated with the formation of singlet oxygen. The latter can react with the photosensitiser itself leading to its own degradation (SATTAR and DEMAN, 1975). Other papers on this topic were quoted in the previous review (BOSSET *et al.*, 1993a). The first-order rate constant for riboflavin loss in whole milk exposed to a light intensity of 1614 lux was about four times higher that in Leben, a fermented dairy product (SAIDI and WARTHESEN, 1993). No further recent reports dealing with the light induced decay of riboflavin have been found.

Most studies are dedicated to the identification of the induced off-flavour compounds as well as the reaction mechanisms of antioxidants, such as ascorbic acid or α-tocopherol, to avoid or delay the formation of degradation products due to oxidation. The occurrence of an off-flavour in milk exposed to light was described long ago (SATTAR and DEMAN, 1975). The so-called “sun-light” or “burnt feather” flavour occurring after an exposure of milk to visible or UV radiation was related to the oxidative degradation of its sulphur-containing protein fraction, and the “card board” flavour, which appears after a more prolonged exposure to the light, was related to the oxidation of the lipid fraction (DIMICK and KILARA, 1983; KIM and MORR, 1996; MARSILI, 1999). UHT milk stored in polyethlyene containers at 6°C under a 36 W vertical light tube was very oxidised and rancid after 4 weeks, while milk stored in a non-foil, paper based barrier carton was only slightly oxidized after 8 weeks and milk packaged in aluminium-foil cartons was not oxidized (RYSSTAD *et al.*, 1998). Analyses of volatile components found in the headspace of milk exposed to fluorescent light over 12, 24 and 48 h have shown a steadily increasing concentration of methional, hexanal, pentanal, dimethyldisulfide, which is directly related to the amount of oxygen available (KIM and MORR, 1996). Likewise, in a comparison of cream powders stored for 35 weeks at 30°C either in darkness or exposed to fluorescent light, the rate of hexanal production was shown to be strongly influenced by the exposure to light and the presence of oxygen in the headspace (ANDERSSON and LINGNERT, 1998). In ice cream stored at – 25°C under a 40 watt “cool white” fluorescent light, the intensity of oxidised flavour was greater on average than in ice creams stored in the dark (SUTTLES and MARSHALL, 1993). Cream packaged in polypropylene- or polystyrene-cups with a polypropylene- or aluminium lid and stored under 950 lx up to 3 weeks was no longer sensorily acceptable after only 3 to 6 days (Anonymous, 1997; SPENGLER, 1997). Whole milk powder stored for 130 days at room temperature under normal daylight contained higher concentrations of volatile lipid auto-oxidation products than milk powder stored at 30°C in the dark (ULBERTH and ROUBICEK, 1995).

More precise kinetic studies of oxygen depletion in headspaces over model systems (water/acetone) which included riboflavin, vitamin D_2 and a protective agent (α-tocopherol or ascorbic acid) and where the model systems were exposed to light (tungsten, 4000 lx) have pointed to the strong relationship existing between oxygen depletion and the amount of vitamin D_2 available as target substrate. The amount of oxygen present in the headspace of the packaged sample did not change in the absence of light. The loss of oxygen was totally correlated with the presence of riboflavin (LI and MIN, 1998) thus confirming the cycle described in *figure 4*. The quantification of the depletion of oxygen demonstrated that both ascorbic acid and α-tocopherol act as quenchers of singlet oxygen, the latter being twice as efficient as the former. They do not prevent the formation of singlet oxygen, but act as quenchers and so compete with the target substrate showing a higher effect at low concentrations of vitamin D_2 (KING and MIN, 1998).

Sensory analysis shows apparently chocolate yoghurt to be much less sensitive to light induced off-flavour degradation than plain or strawberry (BOSSET and GAUCH, 1988). However, further investigation of milk samples containing chocolate leads to the conclusion that this results from a masking effect mainly due to the chocolate flavour itself (CHAPMAN *et al.*, 1998). Chocolate milk could afford some protection against light by filtering it, thus reducing the loss of vitamin A during light exposure. However the degradation of vitamin A is not related to reactions with free radical or singlet oxygen activity (BERGE *et al.*, 1987) but to a direct photochemical process. Moreover chocolate milk contains additional antioxidants such as α-tocopherol (free radical scavenger and singlet oxygen quencher) originating from cocoa and vanillin, which may contribute to some extent to protect chocolate milk against light induced degradation (YANG and MIN, 1994). Retinol can complex with β-lactoglobulin. In this form retinol as well as retinoic acid are more stable to light-induced oxidation by UV-light irradiation than the corresponding free forms (SHIMOYAMADA *et al.*, 1996).

In cheese, the photoinduced decay of vitamin A is not dependent on oxygen while the simultaneous decay of riboflavin is dependent on oxygen, and is located essentially at the surface (MARSH *et al.*, 1994), confirming the measurements in milk. The headspace volatiles and the colour of shredded Cheddar cheese can be influenced by the exposure to fluorescent light and by the atmosphere in the package. Cheeses were packaged under atmospheres of 100% carbon dioxide or 100% nitrogen and stored at 4°C under fluorescent light for 6 weeks. Light-induced oxidation in shredded Cheddar cheeses was more pronounced under carbon dioxide than under nitrogen atmospheres, as evidenced by aldehyde and fatty acid headspace volatiles measured following storage. Only cheeses packaged under carbon dioxide and exposed to light showed colour bleaching. It is proposed that this change is due to an interaction between carbon dioxide and high-intensity light, leading to the oxidation of the pigment molecule, bixin (COLCHIN *et al.*, 2001).

Ascorbic acid (vitamin C) plays a complex role in milk resulting from its opposite actions as an antioxidant, due to its capacity to quench singlet oxygen and free radicals and to regenerate tocopherol radicals, and as a reducing partner of metal ions (Fe^{3+} or Cu^{2+}) (ascorbate$^-$ + $Fe^{3+} \rightarrow Fe^{2+}$ + ascorbate$^\bullet$). In their reduced forms the latter are involved in the formation of aggressive radical hydroxyl HO· according to the reaction:

$$H_2O_2 + Fe^{2+} \rightarrow HO^\bullet + HO^- + Fe^{3+}$$

Superoxide dismutase can also play a role in reducing superoxide anions, which are produced by riboflavin in the presence of light.

The protective effect of ascorbic acid on photoinduced riboflavin degradation was confirmed by measuring the decay of riboflavin upon exposure to light (3300 lx) in whole milk and skim milk (LEE *et al.*, 1998). In the presence of riboflavin the rate of destruction of ascorbate in milk was found to be proportional to the amount of light exposure (SAHBAZ and SOMER, 1993). The riboflavin-sensitised alteration of β-lactoglobulin was reduced by ascorbic acid (0.25-1 $g{\cdot}L^{-1}$) (JUNG *et al.*, 2000). Also, the light-induced reduction of all-trans-retinyl palmitate and 13-cis isomers was inhibited by the addition of ascorbic acid to skim milks (JUNG *et al.*, 1998b). However, the rate of vitamin A loss in fluid milk was not modified by the addition of the ascorbyl palmitate or α-tocopherol (SMITH and BERGE, 1997), but in cream, increased fat content (60 g/100 g) had a protective effect on photodegradation of fortified retinyl palmitate compared to lower fat content (25 g/100 g) (MURTHY *et al.*, 2001). The formation of dimethyldisulfide was also reduced by ascorbic acid (JUNG *et al.*, 1998a). In milk, superoxide dismutase reduced the riboflavin-induced photo-oxidation during storage (LEE, 1998).

4.2 Lipid oxidation

Lipid peroxidation under light exposure has been demonstrated to be not riboflavin dependent but to be more sensitive to short wavelengths from 436 to 366 nm. β-carotene provides good protection against lipid peroxidation by visible light as well as against riboflavin degradation in a model dairy spread (water-in-oil emulsion) (HANSEN and SKIBSTED, 2000). In such a system, the protection of riboflavin is due to the absorption of the light by the carotene. Outside the absorption band of this compound, i.e. at shorter wavelength (366 nm), this protective effect disappears, clearly showing an absorption (filter) effect of the incident light and not a quenching effect of radical or singlet oxygen.

Oxygen free radicals and other reactive oxygen species can be formed in food systems and in the human body. Lipid peroxidation is a major concern of food manufacturers (HALLIWELL *et al.*, 1995). Unsaturated fatty acids are often the target for free radical attack followed by addition of oxygen to form peroxides or hydroperoxides as demonstrated by several studies on milk and other dairy products (MIN and LEE, 1996; YASAEI *et al.*, 1996). The influence of light on the stability of fatty acids and the protective effect of tocopherol (KAMALELDIN and APPELQVIST, 1996) and ascorbic acid (NIKI, 1991) have also been measured in plant oil based fatty acid methyl esters (SIMKOVSKY and ECKER, 1998). Milk packaged in clear pouches and stored under fluorescent light contained significantly higher levels of hexanal and of thiobarbituric acid reactive substances (TBARS) compared to milk packaged in opaque pouches, paperboard boxes or gallon jars (ERICKSON, 1997). In annatto-coloured cheese exposed to cool white fluorescent light with an intensity of 3500 lx, lipid oxidation varied as a function of the pigmented films used (HONG *et al.*, 1995) and this exposure resulted in measurable pink discolouration (HONG *et al.*, 1996). Annatto in a buffer system was more light sensitive than β-carotene and the colour intensity in annatto-coloured Cheddar cheese decreased more than in cheese coloured with β-carotene (PETERSEN *et al.*, 1999). In iron-fortified cheeses the TBARS numbers are increased in the surface layer after exposure to fluorescent light for 28 days (ZHANG and MAHONEY, 1990). During the early phase of the storage of processed cheese (up to 11 days), the formation of radicals was more dependent on light exposure than on temperature (KRISTENSEN and SKIBSTED, 1999). Sliced Havarti cheese exposed to light from Philips TLD 18/83 18 W fluorescent tubes with a light intensity of 1000 lx showed a significant decrease in riboflavin content after storage for 11 days, and the loss reached 60% on day 21. Even if lipid oxidation, monitored by the peroxide value, was not different between cheeses stored under light or in the dark, the effect of light exposure on all sensory attributes other than sour odour (sweet, buttery, rancid odour or taste and sour taste) was significantly different (KRISTENSEN *et al.*, 2000).

Recent work on cholesterol oxidation in butter has shown that exposure to special fluorescent light ("day light" or "natural light") was more damaging than warm light (HIESBERGER and LUF, 2000). However such effects have only been observed after very long exposure to light (several weeks under 300 lx) whereas in all cases butter samples were sensorily completely unacceptable. Under normal storage condition (4°C, packaging protection against light), the formation of these cholesterol oxidation products (7α- or 7β-hydroxy cholesterol) could not be detected under severe light exposure. Exposure of cheeses to fluorescent light for 2 months at 6°C with cool white light oxidized only a small amount of the cholesterol in the cheese (ROSE-SALLIN *et al.*, 1997). Vacuum-packaged cheeses stored for 14 days at 8°C under cool white fluorescent light and covered with burnt orange films had lower thiobarbituric acid values than cheeses covered with clear, sunburst or clear forming films (HONG *et al.*, 1995).

Some experimental differences observed in the kinetics of free radical concentration, riboflavin decay, oxidation production between food in the liquid state (milk, yoghurt) and solid state (hard cheese) (KRISTENSEN *et al.*, 2000) could be explained by their difference in water content. The diffusion of the reactive chemical species (radicals, singlet oxygen, secondary radicals) inside the food can strongly influence the kinetics of degradation of lipid, off-flavour compound formation, and riboflavin decay.

5 – INTERNAL AND EXTERNAL FACTORS INFLUENCING MILK PHOTOSENSITIVITY

Milk processing conditions can significantly influence the photosensitivity of the milk (GALLMANN and EBERHARD, 1993). The harsher the heat treatment applied, the lower the light induced degradation (SAIDI and WARTHESEN, 1995). This observation could be explained by effects such as the size of the suspension particles and the rate of production of sulphur-containing reducing agents (monosulfide). These effects can explain the particularly high sensitivity of skim milk towards light, the reduced fat content of skim milk decreasing its scattering capacity in the visible range. Increased content of transition metal ions ($Fe^{3+/2+}$, $Cu^{2+/1+}$) in milk increases the sensitivity of the milk towards both oxygen and light whereas increased content of reducing agents such as α-tocopherol or ascorbic acid decreases this sensitivity.

Table 2

Internal and external factors affecting the photosensitivity of milk and dairy products towards visible light

Factors	Photopreventive action	Photosensitising action
Intrinsic factors (generally properties of the product itself)		
Structure, texture	compact, scattering	translucent
Own colouration	dark	colourless, bright
Content in	reducing substances/ antioxidants	(pro)oxidants
– vitamins	C (ascorbic acid)	B_2 (riboflavin)
– unsaturated fatty acids	—	peroxide formation
– fat	photodiffusion	degree of unsaturation
– heavy metals	—	catalysis (e.g. Cu^{++})
– dissolved O_2	reducing microflora	synergy with light
– free amino acids (proteolysis)	—	formation of methional
Heat treatments:	harsh	gentle
pasteurisation, UHT treatment, etc.	formation of – SH (= reducing)	formation of -S-S- (= oxidants)
Mechanical treatment:		
homogenisation	?	?
Extrinsic factors (to be considered)		
Source of light		
spectrum UV (λ < 350 nm)	"cut-off" (material)	—
source: day light	—	high energy available
source: artificial light	"white warm"	"white cold"
light (= intensity)	weak	strong
duration of the exposure	short	long
Geometry		
distance from the source	great	short
presentation, disposition of products	closely packed	dispersed
possible auxiliary means	framed crate, baskets	—
Packaging		
light transmission of packaging	weak/zero	high
– with colouring	brown-red	blue-green
– with pigmentation	turbid/light scattering	translucent
material thickness	thick	(ultra)thin
oxygen permeability	weak/zero	high
Storage		
effect of temperature on:		
– O_2 solubility	room temperature	low
– activation energy	low	room temperature
shelf life	short	long

Furthermore, several conditions have to be met in order to protect a food sufficiently against photo-oxidation. Among them, the storage conditions, the emission spectrum of the light used, the transmission spectrum as well as the oxygen permeability of the packaging material play key roles. *Table 2* summarises the main internal and external factors affecting the photosensitivity of milk and dairy products in the visible range.

The first factor to be considered is the choice of the light source. The emission spectra of some commercial fluorescent lamps were presented previously (see *figure 3* in BOSSET *et al.*, 1993a). Fluorescent tubes provide narrow spectral lines with a relatively weak total irradiance (the surface under the spectrum curve) as well as a broad emission which is generally polychromatic (white) light.

The type of light used in storage rooms as well as the exposure geometry and duration determine the degree of light induced degradations. Fluorescent tubes having a strong violet, blue and green emission in the 400-460 nm range produce a "cold" light (more white) and should be absolutely avoided. "Warm white" lamps, richer in yellow, orange and red emission bands are preferred because they minimize the overlapping of the emission band with the third absorption band of riboflavin. It has been observed e.g. that formation of oxidation products in milk is more extensive when a special "Natura" lamp rich in blue-green at 440 nm is used than when a lamp emitting in the red region (OSRAM, 2000), recommended for food presentation, is used (HIESBERGER and LUF, 2000). The warm white fluorescent tube supplied by Osram had a lower emission in the blue-green region (420-460 nm) than the "daylight" white or the Natura, Fluora or Biolux lamps which all contain high irradiance in this region.

6 – NEW PACKAGING MATERIALS AS PHOTOPROTECTORS

The development of new polymer packaging materials led to several studies concerning their light transmittance (CLADMAN *et al.*, 1998; SMELTZ and BARNARD, 1992) and oxygen permeability (METTE, 2000; WANG *et al.*, 1998). Clear polyethylene pouches have a high light transmittance in both UV and visible regions of the spectrum. Therefore, milk packaged in such a material produced a detectable oxidised off-flavour already after 24 h exposure at 1600 lux. A co-extruded black/white polyethylene over-wrap and an over-wrap completely coated with aluminium ink both transmitted less than 3% of light in the visible and UV spectra. Milk stored using these two over-wraps does not suffer from i) oxidised off-flavour development, ii) extensive riboflavin loss, and iii) a high value in the thiobarbituric acid test even after 10 days exposure to fluorescent light (CHRISTY *et al.*, 1981). Under the same light exposure conditions, milk packaged in high-density polyethylene (HDPE) plastic bottles developed a stronger off-flavour than milk packaged in paperboard cartons (HAISMAN *et al.*, 1992). More recently, several clear, green polyethylene terephthalates (PET) including a UV blocker, were compared for their protective action against lipid oxidation and vitamin A degradation in milk stored at 4°C (CLADMAN *et al.*, 1998). Green PET affords better light protection against lipid oxidation and loss of vitamin A in milk, but no measurement of the riboflavin content in this milk was carried out. The UV blocker slowed down the decay of vitamin A as is to be expected from its absorption spectrum. Cutting off the visible light inhibits both lipid oxidation and vitamin A degradation. PET packaging also has high gas permeability. Therefore different treatments or additives were developed to improve its gas-barrier effect towards oxygen and carbon dioxide (DECARNE and DARRAS, 2000; DURAIRAJ, 1999). Treatment of this polymer at high temperatures, such as sterilisation, can however increase its oxygen permeability (TACKER, 1999).

Light transmission spectra of colourless transparent PET bottle for soft drink and brown translucent PET bottle for Rivella are shown in *figure 6*. The first graph presents full light transmission down to 320 nm. The brown PET only has absorption peaks at approximately 450 nm and 680 nm still leaving more than 30% light transmission between 370-420 nm where the third absorption band of riboflavin is located. Even in the lowest transmission range, more than 15% of the light goes through the package which is unable to protect foods containing riboflavin.

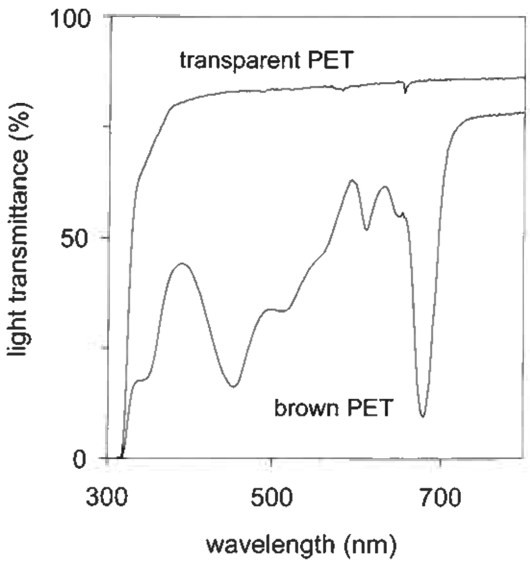

Figure 6

Light transmission spectra of colourless transparent PET for soft drink and brown PET bottle for Rivella bottles

Chitosan is a natural polymer currently proposed as potential edible packaging material with excellent oxygen barrier properties (CANER *et al.*, 1998). Active packaging, with oxygen scavenging technology or release of anti-oxidant, is under development (VERMEIREN *et al.*, 1999). *Figure 7* highlights the possible use of very efficient UV blockers to protect foods against photo-oxidation, especially those sensitive to the UVB region such as ham and sausages.

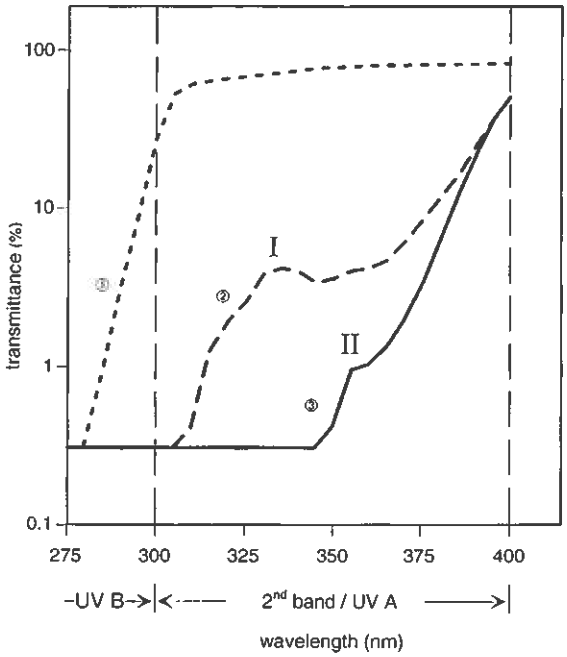

Figure 7

Transmission spectrum of various films in the near UV range
- - - without UV absorber, - - with UV absorber (type I), - with UV absorber (type II).

7 – CONCLUSION – PRACTICAL MEASURES FOR REDUCING PHOTO-OXIDATION

A good knowledge of reaction mechanisms responsible for the photodegradation of foods, particularly milk and dairy products, makes it possible to reduce or even avoid such a risk and the related losses of nutrients.

To reach this goal, the following factors have to be considered:

1. Choice of a mild soft light source: "warm white" fluorescent lamps are to be preferred to "cold white" ones.
2. Choice of an opaque or at least an only partially translucent packaging material to protect the vitamin A content of the stored food as well as the content in vitamin B_2 (riboflavin), the latter being a very efficient light sensitiser.
3. Choice of a packaging material which is gas-tight or at least one which has low oxygen-permeability to prevent or reduce inducing (photo)-oxidation in the stored food, since the presence of oxygen is essential, at least in low concentrations, for oxidation reactions to occur.
4. Choice of the shortest possible duration as well as of the lowest possible intensity of light exposure as well as of the lowest possible storage temperature.

However, the specific sensitivity of the food should also be kept in mind and overprotection is not necessary:

- cream and full-cream milk are less light sensitive than low fat and skim milk due to their greater light scattering properties;
- sterilised or UHT (direct or indirect processed) milks are less photosensitive than raw or low pasteurised milks due to their higher content in monosulfide groups;
- chocolate- and coffee-containing yoghurts are much less photosensitive than plain yoghurts due to their light absorbing properties as well as to the antioxidants which they contain. In general, high content in reducing agents such as vitamin C, tocopherol and polyphenols is photoprotective while high content in oxidising agents such as copper and iron ions induces and enhances oxidative degradation.

Before choosing a (new) packaging material, a preliminary assay should always be carried out to evaluate the risk of photo-oxidation by exposing the particular food for a few days to an intense known cold white light source (THRON and ZIEGLEDER, 2001). For such accelerated trials, sensory tests and HPLC determination of the riboflavin content are low cost and rapid indicators of food photosensitivity, thus leading to valuable conclusions for the choice of the most suitable packaging material (BOSSET and FLÜCKIGER, 1989).

The current review highlights the great complexity of the photo-oxidation of milk and dairy products. Several new publications have dealt with particular aspects of this topic. A general need for the future is computer modeling which will certainly help to predict the shelf life of food products for the optimisation of packaging (PFEIFFER *et al.*, 1999). Maximum packaging protection is not usually the most cost-effective solution. It therefore makes sense to design packaging not only for maximum product protection but also for a defined shelf life.

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