OXYGEN SCAVENGING PACKAGING SYSTEMS

Introduction

Oxygen scavengers are mainly used for food and pharmaceutical applications, but can also be used for any product that needs a low oxygen storage atmosphere. Essentially, oxygen scavengers are so named because they preferentially absorb oxygen within the environment, thus, preventing the oxygen from reacting with the product. Many other terms have been used to describe oxygen scavengers, which include the following: antioxidants, interceptors, controllers, and absorbers. According to Brody, the definition of an oxygen scavenger is a material in which a chemical (or combination of reactive compounds) is incorporated into a package structure and may combine with oxygen to effectively remove oxygen from the inner package environment (1). The purpose of an oxygen scavenger is to limit the amount of oxygen available for deteriorative reactions that can lead to reduced functionality of the product. For foods and pharmaceutical products, deteriorative reactions include lipid oxidation, nutritional loss, changes in flavor and aroma, alteration of texture, and microbial spoilage. Typically, oxygen scavengers are used in packages that have air tight seals and are used in conjunction with other means of preservation, such as chemical preservatives, reduced water activity, reduced pH, vacuum packaging, or modified atmosphere packaging.

History

Research on oxygen scavengers began in the 1920s for enclosed packages using a ferrous sulfate and moisture absorbing mixture (1). A British patent from 1938 used iron, zinc, or manganese to scavenge oxygen from canned foods (2). Research continued throughout the 1940s with the bulk of the work performed in the United Kingdom and by the U.S. Army for military rations. During the 1970s, the first major commercial oxygen scavenger was introduced by Mitsubishi Gas and Chemical Company in Japan, which was available in the United States by the late 1970s. The product eventually became known under the trade name Ageless and functions by using a permeable sachet that contains a reduced iron salt and moisture absorbent material. Toppan Printing Company in Japan also produced a commercially available oxygen scavenging system, but it functioned using an ascorbic acid-based reaction. During the 1970s and 1980s, more oxygen scavenging systems were introduced by Japanese and U.S. companies using several scavenging methods (1,2). During the 1980s, work began on oxygen scavenger

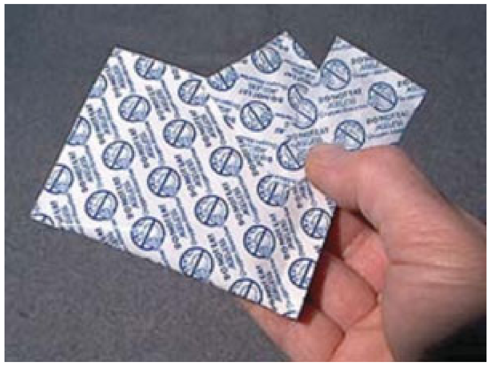

Fig. 1. Mitsubishi ageless sachets.

development using singlet oxygen reaction by the Commonwealth Scientific Industrial Research Organization (CSIRO) in Australia. (See sachets shown in Figs. 1 and 2).

Oxygen scavengers are the most patented of all active packaging technologies with at least 50 patents through 1989 and 20 issued from 1990 to 1994 (3). In the 1990s, work focused more heavily on technologies to incorporate oxygen scavengers directly into film and other package forms such as closure liners, thermo-formed cups, tubs, and trays rather than sachets. Part of the reason for this change was related to concern over consumers accidentally using the sachets as “flavor packets” and incidents whereupon the contents of the sachet may seep out into the food. These problems can lead to loss of product quality and can

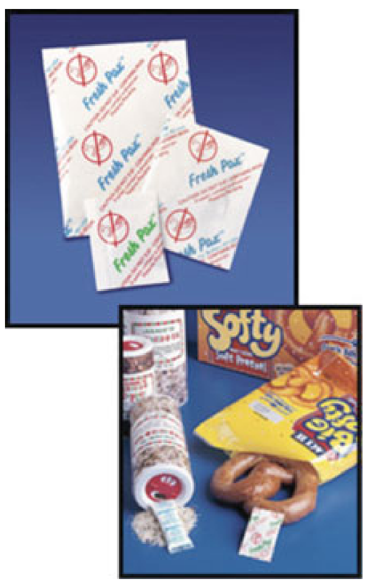

Fig. 2. Multisorb Freshpax.

also lead to serious consumer safety concerns. For example, iron in concentrated amounts can be toxic to children or pets, because of their small body mass. For this reason, the U.S. Food and Drug Administration mandated that iron-based sachets must be labeled with "Do not eat" on the sachets sold in the United States to avoid accidental ingestion of the contents. (4).

Based on information made available in 2002, oxygen scavengers in bottles made up the largest portion of the market with 43.8% of the market, followed by cap/liner/lidding representing 31.5%, sachets with 22.6%, and oxygen-absorbing film with 2% (5).

Types and Mechanisms of Action

Iron-Based Systems. Iron-based sachets are the type of oxygen-scavenging system that has been used commercially for many years. It generally involves a reaction between iron powder contained in a permeable sachet that also may contain a desiccant. Iron powder reacts with oxygen using the following reactions (6,7):

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$\frac{1}{2}\,O_2 + H_2O + 2\,e^- \rightarrow 2\,OH^-$$

$$Fe^{2+} + 2\,OH^- \rightarrow Fe(OH)_2$$

$$Fe(OH)_2 + \frac{1}{4}\,O_2 + \frac{1}{2}\,H_2O \rightarrow Fe(OH)_3$$

Oxygen Scavenging Polymer Materials. Many polymers have been developed using a wide variety of chemistries (2); however, the most commercially successful materials have been homogeneous blends of reactive substances with polymers. An effective oxygen scavenging polymer was developed in which dissolved reagents of known chemistry were incorporated into a polymer, and the trigger mechanism was light, which excited the reactive components in the film, thus, influencing oxygen diffusion into the polymer. The oxygen has to be in an excited singlet state, which requires the use of a photsensitizing dye and exposure to visible light. Another approach was based on transition-metal-catalyzed oxidation of an aromatic nylon. The transition metal in this case was cobalt or cobalt salt. This material eventually became known under the trade name, Oxbar. The material easily could be blended with polyester and eventually became important for packaging wine and beer in plastic bottles, because it could effectively prevent oxidation in both products. Amoco Chemicals introduced a material called Amosorb, which blended polyester and polybutadiene and was catalyzed by a transition metal salt. When the catalyst was added late in the injection-molding process, the resulting material became an oxidizable polymer. Another material using light as a triggering mechanism was developed and used a transition metal catalyst and a photosensitizer (8). The reaction was designed in such a way as to prevent the rupture of the polymer backbone as might normally occur through

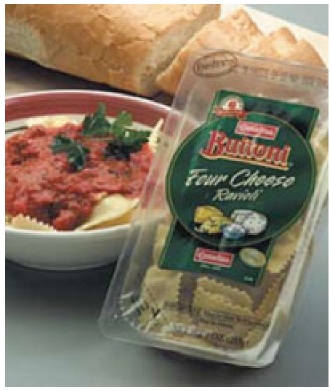

Fig. 3. Cryovac OS1000 oxygen scavenging film.

oxidation. The material was composed of unsaturated polymers such as poly(1,2-butadiene), which could scavenge ground-state oxygen as opposed to singlet oxygen. This product is marketed under the trade name OS 1000 or 2000 by Cryovac Division of Sealed Air (Fig. 3).

Other materials that incorporate active components into the polymer include material marketed by Chevron Chemical Company, which works by autooxidation of unsaturated groups on the polymer backbone. Oxidation of aromatic nylons and hydrocarbon polymers with active side groups use light to trigger the oxygen scavenging process. One method that differs from the light-triggering systems involves the light excitation of a photoreducible component such as phenolic compound, which is reduced by oxygen, thereby scavenging oxygen.

Designing an oxygen scavenging system for specific types of packaging is quite complex and still not well understood except by the vendors who specialize in such systems. Most oxygen scavengers are designed for packaging based on the removal of a specified amount of oxygen from the interior of the package over a period of a few days. The oxygen absorption kinetics of six commercial oxygen scavengers that differed in oxygen scavenging capacity as well as oxygen scavenging methods (ie, iron based and enzyme based) was studied (9). It was determined that the oxygen concentration was the primary limiting factor in the kinetics of oxygen scavengers in atmosphere of less than 500 ppm but other factors such as temperature, capacity, and variation between types of scavengers also occurred. Miltz and Perry (10) studied the performance of iron-based oxygen sachets to improve methods of applying them more effectively since cost and the lack of technical understanding have limited their use. Based on their study, the actual scavenging capacity was higher than the manufacturers specifications. They also found that, in modified atmosphere packages containing carbon dioxide, the sachets also absorbed the carbon dioxide as well as oxygen. Oxygen sachets were found to reduce the transient period time (time to reach equilibrium) for active modified atmosphere packaging by nearly half compared to passive modified atmosphere packaging without a sachet. This effect allowed the shelf life to be extended because of optimal atmosphere as soon as quickly as possible (11).

Applications

Current Use. Oxygen scavengers were initially used by the U.S. military for the meals ready to eat (MRE) rations. Foods with oxygen scavengers for MREs include the following: white and whole wheat bread, pound cake, fudge brownies, wheat snack bread, potato sticks, chow mein noodles, nut raisin mix, pretzels, waffles, and hamburger buns (1). In the retail market, typical uses in the United States include fresh pasta, beef jerky, pepperoni, beer (cap liner and some bottles), ketchup, juice, case-ready meats, prepared foods, and shredded cheese. Use of oxygen sachets is more prevalent and diverse in Japan for products such as seasonings, cheese, aseptically packaged cooked rice, dry pet foods, cough capsules, plant growth hormone, antibiotics, vitamins pills and tablets, medical kits to preserve reagents, kidney dialysis kits, and other products.

Current Research.

Meat Packaging. Oxygen scavengers are used in meat packaging to control color in red meat packages. When the pigment for red meat (myoglobin) is exposed to oxygen, the meat appears as a bright red color, which is associated with freshness and overall acceptability. However, when meat is exposed to too much oxygen over time, the pigment converts to metmyoglobin, which appears as a brown color and is not visually acceptable to consumers. Many studies have used oxygen scavengers in modified atmosphere packages to extend the display life of red meat packages. The conditions under which commercially available scavengers with an oxygen absorbing capacity of 200 mL/sachet could prevent transient discoloration of nitrogen flushed ground beef were studied (12). The rate of oxygen absorption decreased with decreasing oxygen concentration when the oxygen concentration was between 10% and 20%, but the rate of oxygen absorption became exponentially proportional with time when the oxygen concentration was less than 1%. Oxygen concentration in packages needed to be reduced below 10 ppm in 30 min at 2°C or 2 h at 1.5°C to prevent transient discoloration. It was determined that to achieve this, more sachets than were economically feasible would have been required at that time. Continued work on prevention of transient discoloration of beef was done by Tewari and others (13), who determined that steaks removed from a controlled atmosphere masterpack had less discoloration when packaged with an oxygen scavenger and that the number of sachets had more impact on discoloration prevention than the type of scavenger used. The same research group also studied the effect of oxygen scavengers inside retail trays, lidding and over-wrapped trays, which were all equally effective for extending the acceptable shelf life of modified atmosphere, display ready beef, and pork cuts (14). They also found that eight oxygen scavengers with a capacity sufficient to achieve an oxygen half life of 0.6–0.7 were needed when oxygen concentration could otherwise remain at less than 500 ppm during storage. The redness of meat 96 h after removal from a gas-flushed mother pack was measured (15). It was found that redness of meat packaged in a retail tray containing oxygen scavengers was better than retail trays that did not contain an oxygen scavenger. In another study, researchers found that a tray combined with a controlled atmosphere mother pack (outer bag), double-flushed with 50% carbon dioxide and 50% nitrogen was effective for maintaining the display shelf life of variety of red meat cuts (16). The oxygen scavenger helped maintain a low level of oxygen (0.1%) to prevent formation of metmyoglobin.

Another study involved vacuum-controlled atmosphere packaging with carbon dioxide, carbon dioxide flushed packages containing iron-based oxygen scavenging sachets, and packages that contain oxygen scavengers alone for beef stored for up to 20 weeks at –1.5°C (17). Beef packaged with oxygen scavenger alone provided the best results with regard to drip loss, microbial, and sensory properties. Fresh pork sausages packaged in a 20% carbon dioxide, 80% nitrogen atmosphere with an iron-based oxygen scavenging sachet, were found to have had reduced psychrotropic aerobic counts and extended shelf life with regard to color and lipid stability for 20 days at 2°C (18). Catfish steaks were packaged in barrier film and vacuum packaged with and without an iron-based sachet. Shelf life was extended 10 days (20 days with sachet vs 10 days without sachet) with the aid of the sachet based on sensory, microbiological, and volatile base nitrogen analysis. The oxygen in the packages containing the sachets reached 0.42% within 24 h of packaging (19). Labels are manufactured that absorb 10–20 mL of oxygen, and larger labels are starting to become available that scavenge 100–200 mL O_2 (7). Besides labels, oxygen scavengers can also be incorporated into the polymer film. The film is capable of reducing oxygen in the headspace to less than 1 ppm in 4–10 days for products such as dried, smoked meat, as well as processed meat products (20).

Bakery Products. Baked goods such as bread, pastries, cakes, and cookies can have an extended shelf life with use of oxygen scavengers combined with modified atmosphere packaging. The low-oxygen condition retard molds and other spoilage bacteria and also reduces lipid oxidation, which can produce off flavors. An advantage over using an oxygen scavenger system compared to modified atmosphere packaging alone was because of the fact that lower oxygen levels could be achieved, and oxygen can be reduced in the case of leakage through defective seals (21). The disadvantages could be cost and possible consumer objection to a packet inserted inside the package that could become loose and cause accidental ingestion by a child or pet. A few studies have reported on the effectiveness of oxygen scavengers for bakery products. Sponge cakes (0.8–0.9 a_w) were packed in a modified atmosphere package with oxygen absorber sachets of two different absorption capacities (100 and 210 mL). The cakes were analyzed for mold growth over a period of 28 days at 25°C storage. Modified atmosphere package alone provided some benefits regarding mold prevention; however, combining oxygen scavengers (using either 100 or 210 mL) with modified atmosphere (30% CO_2) prevented mold growth entirely during the 28 days of storage. The results also indicated that a greater benefit existed for cakes with a higher a_w (0.9) compared to lower a_w (0.8) (22).

In another study, oxygen absorbers were added to wheat crackers formulated with high levels of oil for storage in hermetically sealed cans used as military rations. The study included storage at 15, 25, and 35°C (23). Shelf life was assessed using sensory panels as well as hexane concentration and headspace oxygen measurements. As storage temperature increased, headspace oxygen decreased within the can. Overall, cans of crackers without oxygen sachets reached unacceptable levels of rancidity within 24 weeks at 25 and 35°C. Cans of crackers with oxygen sachets did not have rancid odors after 44 weeks of storage, regardless of storage temperature. Thus, shelf life of canned crackers was extended for 20 weeks with oxygen absorbers added to the can.

Other Products. Orange juice contained in aseptic packages with an oxygen scavenging barrier layer was found to have better retention of ascorbic acid than packages with plain oxygen barrier film (24). Packages that contained oxygen scavengers had less mold growth on cheddar cheese compared to packages without the oxygen scavengers over a 16-week refrigerated storage period (25).

Milk processed using ultra-high temperature processing, was packaged and stored in aseptic pouches that contain an oxygen scavenging film or a pouch without the scavenging film. The milk in the oxygen scavenging pouch had significantly lower levels of dissolved oxygen and levels of volatiles associated with staleness (26). Hazelnuts were packaged under controlled atmosphere conditions with and without iron-based oxygen sachets. The nuts packaged using the sachets were significantly less oxidized compared to the nuts without the sachets. However, when the sachets were analyzed for volatile compounds, other flavor compounds were also scavenged by the sachets (27).

Regulations

A program was developed by the European Union (EU) Fair R&D program to establish and implement active and intelligent packaging technologies within existing EU regulations, which would enable technologies to be used and allow for products to be globally competitive with other technologies. The program included, inventory, classification, evaluation, and recommendations for regulation of active and intelligent packaging systems. Oxygen scavenging systems were examined as part of the evaluation step and were tested for migration into a variety of food stimulants. It was determined that migration from oxygen scavengers varied significantly depending upon type of system (sachet, cap, crown, or film) and food stimulant (3). For example, migration of oxygen scavenger in water (mg/sample) was 620, 74, 1.0, and 0.2 for sachet, cap, crown, and film, respectively. Migration into liquid, solid, and gelled food stimulants using two different types of oxygen sachets was tested (23). Migration from oxygen scavengers did not exceed E.U. migration limits as long as the sachet was properly located in the package, and the packaging process did not favor the content becoming wet from water released from the food.

Future Considerations

New methods of producing oxygen scavengers will continue to be developed. For example, the use of aerobic microorganisms as the mechanism for oxygen scavenging has been suggested (29). The microorganisms can be trapped in poly(vinyl alcohol) and used as a coating for high humidity foods. Another use that may see increased application is addition of an oxygen sachet with biopolymer film. Poly(lactic acid) film did not have oxygen barrier properties equal to the polyester film typically used for packaging semihard cheese (30). However, when an oxygen scavenger was added to the package, lipid oxidation of the cheese was

Table 1. Oxygen Scavenging Components

Sulfites
Boron
Glycols and sugar alcohols
Unsaturated fatty acids and hydrocarbons
Palladium catalysts
Enzymes
Yeast
Ferrous-iron
Organometallic ligands
Photosensitive dyes
Polydiene block copolymers
Polymer-bound olefins
Aromatic nylon

significantly reduced and continued to improve with dark storage (Tables 1 and 2).

Another new method may involve radiation treatment of ethyl vinyl alcohol copolymers. Researchers irradiated ethylene vinyl alcohol (29% ethylene) with 30 and 90 kGy dosages and found that as the dosage increased, the longer the polymer was able to react with oxygen (31).

Oxygen scavengers that function better under a variety of temperatures will also be used. A patent was issued for an oxygen scavenging film that acts under ambient and refrigerated conditions and can be incorporated uniformly into a multilayer film (32). Another development involves a patent that indicates that the activation of the oxygen scavenging component of a film can be triggered upon packaging with the product to prevent loss of scavenging capacity in films that may be active while film is in storage (prior to product packaging). The film would receive an initial trigger using actinic radiation, which would not be sufficient to

Table 2. Commercially Available Oxygen Scavenging Systems

Trade name	Supplier
Agelesss	Mitsubisihi Gas and Chemical Co., Japan
ATCO	Emco Packaging Systems, UK; Standa Industries, France
Freshilizers series	Toppan Printing, Japan
Freshpax	Multisorb Technologies, Inc. USA
Freshmax	
Bioka	Bioka, Finland
Smartcap	ZapatA Industries, USA
Daraform, Cryovac OS 1000	Cryovac, Division of Sealed Air, USA
Oxyguard	Toyo Seikan Kaisha, Japan
Oxbar	Carnaud Metal Box, UK
Zero$_2$	CSIRO, Southcorp Packaging, Australia
Amsorb	Amoco Chemicals, USA

activate the film fully and would receive the total dose necessary to trigger the oxygen scavenging component when desired (33).

An oxygen scavenger that also indicates the level of oxygen present has been developed, which makes it both an active, and intelligent package component. The scavenger is in a pouch form with a layer in the pouch that has a color changing substance that can be viewed through a clear window (34).

BIBLIOGRAPHY

CITED REFERENCES

1. A. L. Brody, E. R. Strupinsky, and L. R. Kline, *Active Packaging for Food Applications*, CRC Press, Boca Raton, Fla., 2001.
2. M. L. Rooney, in J. H. Han, ed. *Innovations in Food Packaging,* Elsevier Academic Press, San Diego, Calif., 2005, pp. 123–137.
3. N. de Kruijf, M. van Beest, R. Rijk, T. Spilainen-Malm, P. Paserio Losada, and B. De Meulenaer, *Food Addit. Contam.* **19** (Supp.) 144–162 (2002).
4. M. Ozdemir and J. D. Floros, *Crit. Rev. Food. Sci. Nutr.* **44**, 185–193 (2004).
5. A. Brody, *Active Packaging: Beyond Barriers*, Packaging Strategies, West Chester, Pa and BRG Townsend, Mt. Olive, N.J., 2002.
6. F. Charles, J. Sanchez, and N. Gontard, *J. Food Eng.* **72**, 1–7 (2006).
7. J. P. Kerry, M. N. O'Grady, and S. A. Hogan. *Meat Sci*, **74**, 113–130 (2006).
8. U. S. Pat. 5,211,875 (May 18, 1993), D. V. Speer, W. P. Roberts, and C. R. Morgan (to W. R. Grace & Co.).
9. G. Twari, L. E. Jeremiah, D. S. Jayas, R. A. Holley *Int. J. Food Sci. Technol.* **37**, 199–207 (2002).
10. J. Miltz and M. Perry, *Packag. Technol. Sci.* **18**, 21–27 (2005).
11. F. Charles, J. Sanchez, and N. Gontard, *J. Food. Sci.* **70**, E443–E449 (2005).
12. C. O. Gill and J. C. McGinnis, *Meat Sci.* **41**, 19–27 (1995).
13. G. Twari, D. S. Jayas, E. Jeremiah, and R. A. Holley, *J. Food. Sci.* **66**, 506–510 (2001).
14. G Twari, D. S. Jayas, L. E. Jeremiah, and R. A. Holley, *Int. J. Food. Sci. Technol.* **37**, 209–217 (2002).
15. E. Isdell, P. Allen, A. Doherty, and F. Butler, *Int. J. Food. Sci. Technol.* **34**, 71–80 (1999).
16. E. Isdell, P. Allen, A. Doherty, and F. Butler, *Int. J. Food. Sci. Technol.* **38**, 623–632 (2003).
17. S. R. Payne, C. J. Durham, S. M. Scott, and C. E. Devine, *Meat Sci.* **49**, 277–287 (1998).
18. L. Martinez, D. Djenane, I. Cilla, J. A. Beltran, and P. Roncales, *Food. Chem.* **94**, 219–225 (2006).
19. C. O. Mohan, C. N. Ravishankar, and T. K. Srinivasagopal, *J. Sci Food. Agric.* **88**, 442–448 (2008).
20. B. Butler, in *Proceedings of Worldpak 2002*, East Lansing, Mich., 2002.
21. I. S. Kotsianis, V. Giannou, and C. Tzia, *Trends Food Sci. Technol.*, **13**, 319–324 (2002).
22. M. E. Guynot, V. Sanchis, A. J. Ramos, and S. Marín, *J. Food Sci.* **68**, 2547–2552 (2003).
23. S. Berenzon and I. S. Saguy *Lebensm.-Wiss. Technol.* **31**, 1–5 (1998).
24. K. Zerdin, M. Rooney, and J. Vermue, *Food. Chem.* **82**, 387–395 (2003).
25. E. Oyugi and E. Mbuy, *Int. J. Dairy Technol.* **60**, 89–95 (2007).

26. M. Perkins, K. Zerdin, M. L. Rooney, B. R. D'Arcy, and H. C. Deeth, *Packag. Technol. Sci.* **20**, 137–146 (2007).
27. S. Pastorelli, S. Valzacchi, A. Rodriguez, and C. Simoneau, *Food Addit. Contam.* **23**, 1236–1241 (2006).
28. J. Lopez-Cervantes, D. I. Sanchez-Machado, S. Pastorelli, R. Rijk, and P. Paserio-Losada, *Food. Addit. Contam.* **20**, 291–299 (2003).
29. C. Altieri, M. Sinigaglia, M. R. Corbo, G. G. Buonocore, P. Falcone, and M. A. Del Nobile, *Lebensm-Wiss. Technol.* **37**, 9–15 (2004).
30. V. K. Holm, G. Mortensen, M. Vishart, M. A. Petersen, *Int. Dairy J.* **16**, 931–939 (2006).
31. A. Lopez-Rubio, J. M. Lagaron, T. Yamamoto, and R. Gavara. *J. Appl. Polym. Sci.*, **105**, 2676–2682 (2007).
32. U. S. Pat. 7,078,100 B2 (July 18, 2006), C. L. Ebner, A. E. Matthews, and T. O Millwood, (to Cryovac Division of Sealed Air).
33. U. S. Pat. 7,238,300 (July 3, 2007), J. A. Solis, R. Dayrit, S. W. Beckwith, B. L. Butler, R. L. Cotterman, D. V. Speer, and T. D. Kennedy.
34. European Pat. Appl. EP 1 676 790 A1 (2006) W. Yang, Y. Yang, and L. Xiuzhi.

GENERAL REFERENCES

M. L. Rooney, in M. L. Rooney, ed., *Active Food Packaging*., Blackie Academic Professional, London, UK, 1995, pp. 145–165; F. N. Teumac, pp. 193–202.

G. Robertson, in G. Robertson, ed., *Food Packaging, Principles and Practices*, 2nd ed., CRC Press, Boca Raton, Fla., 2006, pp. 292–293.

V. Daniel, and F. L. Lambert. Available at http://palimpsest.stanford.edu/waac/wn/wn15/wn15-2/wn15-206.html. Accessed November 7, 2008.

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