



Review article

Particle films and their applications in horticultural crops

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ABSTRACT

Due to rising health concern, the idea of Good Agricultural Practices (GAPs) has emerged, especially for growing crops organically. In this context, several innovative technologies have been developed by agricultural scientists, such as the particle film technology (PFT). They are basically aqueous formulations made from chemically inert clay or mineral particles, which are specifically formulated for coating to reduce the damage caused by insects, diseases, solar injury, freeze injury and to improve fruit finish, color, carbon assimilation rate, yield and postharvest fruit quality. The development of the first such kaolin-based formulation, named Surround®, for commercial use was by Engelhard Corporation, Iselin, New Jersey (U.S.A.) in 1999. During the last two decades, a significant amount of research work has been conducted on the development of several such films (Surround® CF, Surround® WP, Raynox®, Cocoon™, Purshade™, Parasol®, Screen®, Snow®, Eclipse™, etc.) and their effects on various agricultural and horticultural crops. Considering the usefulness of these films, we attempted to compile the scattered information on the developed particle films, their modes of action and effects on various horticultural crops, in the form of a review. The review is particularly focused on history, modes of action, application and a variety of effects of particle films on horticultural crops.

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1. Introduction

With the increasing awareness of consumers about harmful effects of the residues of pesticides, which are used for the production of horticultural commodities, there has been a rigorous search for some alternatives that could help in reducing the use of the toxic chemicals, which are not only a rising concern for the consumer health but also for environmental safety (Sharma et al., 2009). Perhaps, it is this concern that has forced the planners the recommendations of the use of Good Agricultural Practices (GAPs) throughout the world. As a result, several GAPs have been recommended for the production of horticultural commodities. One of the several innovations was the development of processed particle film technology (PFT). This includes the development of aqueous formulations from chemically inert mineral particles, which are specifically formulated for coating over the agricultural and horticultural produce as protective films (Stanley, 1998; Glenn and Puterka, 2004). These particle films exhibit several effects such as reduction in insect and plant pathogen damage, enhancement in the photosynthesis and yield of horticultural products, due to their several basic physical properties (Glenn and Puterka, 2005).

Most of the particle films are based on kaolin, a white, non-porous, non-swelling, low-abrasive, fine grained, plate-shaped, aluminosilicate mineral $[\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8]$, which disperse easily in water and are chemically inert over a wide range of pH (Glenn and Puterka, 2005). This is a secondary mineral, derived from the primary minerals which occur naturally as inorganic substances in the soil and sediments. Mined, crude kaolin contains traces of Fe_2O_3 (ferrous oxide) and TiO_2 (titanium oxide) that are removed during processing to increase its brightness. Water-processed kaolin is >99% pure and has >85% brightness (Glenn and Puterka, 2005). However, crystalline silica, SiO_2 , a respirable human carcinogen, must be removed to ensure human safety (Harben, 1995). With the technical advancement in kaolin processing, it is now possible to produce kaolin particles with specific shapes, sizes, and with light reflective properties (Glenn et al., 2002).

Traditionally, kaolin was used in ceramics, medicine, bricks, coated paper, as a food additive, in toothpaste, as a light diffusing material in white incandescent light bulbs, and in cosmetics and as a filler in many other applications (Glenn et al., 2002). Kaolin has even been used for spiritual and healing purposes. The largest and most common use of kaolin is in the paper industry, where it has been the main ingredient in creating 'glossiness' in the paper. Potential uses of kaolin particles have been ignored by the agricultural and horticultural industry except for its use as carrier for wettable powder formulations of some pesticides. With the increase in interest and knowledge, several

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advances have been made by the scientists in kaolin processing, formulation and plant surface deposition properties, which have opened new avenues for its use as an integral part of organically grown horticultural crops.

2. History of mineral particle film use

In nature, many animals commonly take 'dust baths' to save themselves from insect parasites and attacks from biting insects. Soil dusts have also been used as insect repellents by primitive people, mammals and birds regularly to avoid insect bites (Ebling, 1971). In ancient times, elemental sulfur or sulfur compounds along with bitumen were used to be heated to generate sulfur fumes to repel insects from vines and trees (Smith and Secoy, 1975). In the very early days, diatomaceous earth (diatomite) was used to protect plants from pests in China (Allen, 1972). Since then, there is a long history on the use of various mineral-based preparations, and some of these are still used for special purposes in agricultural or horticultural pest control. Arsenic and arsenic salts were used in China around 900 C.E., and were being incorporated into ant baits in Europe during 1699 (Casida and Quistad, 1998).

During the first century AD, powdered limestone (calcium carbonate) was added to grains for deterring storage insect-pests. A mixture of hydrated lime and sulfur was one of the primary insecticides and fungicides of early agri-horti production systems (Secoy and Smith, 1983). Hydrated lime or sulfur was applied either alone or in combination to protect several agricultural and horticultural crops from insect damage. Furthermore, chemically reactive hydrated lime and sulfur were being applied along with tobacco, wood ash, linseed oil, soap and cow dung as paints or washes to fruit trees and grapevines to protect them from insect and disease damage. Slaked lime [$\text{Ca}(\text{OH})_2$] and burnt lime [CaO] were used against household, stored grain and crop insect pests during the late 1500s to the 1800s. Sulfur in combination with limestone were burnt as a fumigant for trees, while lime-sulfur preparations became popular in the later part of the 18th century, which replaced the application of individual minerals. Thus, in the older time, lime sulfur, slaked lime and sulfur were the main materials for insect and disease control as these were easily prepared.

In the 1920s, use of dust applications over liquid sprays was preferred because of the ease and speed of dusting operations, good plant coverage, economy in labor, and comparable insect control with liquid sprays (Giddings, 1921; Headly, 1921). The increased interest in the use of dusts to deliver insecticides was proposed from research that indicated 'self cleaning' response of chemically active particles of sodium fluoride and borax (Shafer, 1915; Mote et al., 1926), which was primarily due irritation leading to death by the ingested particles. In the 1930s, it was established that certain 'inert dusts' themselves had toxic activity against insects when ingested during the process of self cleaning (Boyce, 1932; Richardson and Glover, 1932).

Insecticidal dusts were used as a primary means of delivering insecticides in the 1940s. Watkins and Norton (1947) found that abrasive dusts like alumina-aluminum oxide (Al_2O_3) or silica oxide (SiO_2) were the best carriers of DDT. Between the 1950s and 1960s, non-abrasive sorptive dusts like montmorillonite and attapulgite were found to remove the thin lipid layer covering the epicuticle of dry wood termites. The ability of finely divided particles to adsorb and remove the cuticular waxes of insects was proved by Ebling and Wagner (1959). Interest in the control of insects with inert dusts has transitioned from minerals to synthetic compounds like silica aerogels and fumed silicas by 1970.

The research on mineral particles after 1970 was limited to pesticide formulations in which mineral particles were used as carriers for synthetic pesticides (Kirkpatrick and Gillenwater, 1981; Margulies et al., 1992) or microbial agents (Studdert et al., 1990; Tapp and Stotzky, 1995) and in the use of minerals as white-wash sprays for preventing plant viral diseases that were spread by aphid vectors (Adlerz and Everett, 1968; Bar-Joseph and Frenkel, 1983) and thrips (Smith et al.,

1972). Mineral based white-washes have been examined for the prevention of insect vectored transmission of plant viral diseases. White reflective surfaces repel certain aphids by affecting their host-finding and settling responses (Kennedy et al., 1961; Kring, 1962).

White-washes come in various forms and are generally composed of kaolinite, bentonite, and attapulgite with the addition of spreading and sticking agents that are designed to white-wash the plant stem, foliage or soil surrounding the plant (Nawrocka et al., 1975; Bar-Joseph and Frenkel, 1983; Marco, 1986, 1993). This approach was successful but was limited to repel aphids and leafhoppers, which act as vector for the spread of several viral diseases of horticultural crops. In the 1980s, kaolin based sprayable mulch was developed and demonstrated to be effective against *Aphis spiraecola* Patch, in citrus (Bar-Joseph and Frenkel, 1983). White-wash spray for insect control couldn't become popular and was of little scientific interest until development of several particle films such as 'Surround', 'Cocoon', 'Parasol', 'Purshade', 'Screen', and 'Eclipse', which have led to new possibilities for its use in agricultural related activities.

3. Commercialization of particle film technology

The wild idea for research on particle film technology was perceived from the fact that mineral particles have a significant influence on insect behavior which was not previously recognized (Glenn et al., 1999; Puterka et al., 2000a). As a result, research on particle film was initiated during 1994 with the attempt to control fruit diseases with hydrophobic kaolin films. Hydrophobic kaolin particle film (M96-018) was co-developed by the United States Department of Agriculture (USDA) and Engelhard Corporation, Iselin, New Jersey, the world leader in surface and materials science, through several years of development.

The film was quite effective against insects and mites on apple and pear but due to problems in its mixing with water and lack of adhesiveness to plant, made it impractical (Glenn, 1999). A year later, a methanol (MEOH)-water system was developed in which hydrophobic film could be pre-slurried and easily sprayed on trees but it was quite expensive and difficult to handle and transport it. Moreover, methanol was listed as hazardous material in the U.S. (Puterka et al., 2000a). Considering these problems, the scientists at the Engelhard Corporation, Iselin, New Jersey, developed hydrophilic kaolin based film, M97-009 which required a non-ionic spreader-sticker, M03. The material in this film was similar to M96-018 but without silicon coating having a particle size of less than $1.0\ \mu\text{m}$ in diameter. This formulation was quite effective in controlling insects and diseases under lab as well as field conditions (Puterka et al., 2000a,b).

Advantages of using the hydrophilic films were: i) ease of mixing, ii) less expensive, iii) good compatibility with other spray materials, and iv) easy spreadability over tree canopy. These formulations (M97-009 + M03) were named as Surround® Crop Protectant and made commercially available in 1999 (Corporation, Iselin, New Jersey). Although this formulation was quite effective against insect-pests but handling and shipping of two package system (particles + spreader-sticker) was quite problematic. Hence, research was focussed for the development of a single package system. As a result, Surround® Crop Protectant was replaced by Surround® WP, which contained kaolin particle with sticker and spreader agents (Glenn and Puterka, 2005). In 2002, Surround® CF was developed and made commercially available which is similar to Surround® WP but has different spreader-sticker which speeds up the mixing at low temperature ($4\text{--}10\ ^\circ\text{C}$).

The developed particle-based formulations offer several important qualities, such as: reflectance of the sun's heat; easy mixability in water; good coverage capacity; and good adherence to the plant canopy and fruit. Now, several particle film formulations such as Surround® (95% Calcined kaolin), Surround® CF, Surround® WP, RAYNOX®, RAYNOX AIR, RAYNOX ORGANIC, Cocoon™ (100% hydrous kaolin), Parasol®, Anti-stress 500®, Purshade® (62.5% limestone), Screen®, Snow®, Eclipse™ (Ca + B), Fruit Shield (Black particles) and Savona®

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