Morpholine: A Glazing Agent for Fruits and Vegetables Coating/Waxing

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Abstract

The saying “an apple a day keeps the doctor away” probably gives us the impression that apples are the healthiest fruits. But besides the fact that it rhymes, does it really have no adverse effects if we eat a bright red wax coated apple every day? Morpholine (C4H9NO) is a chemical used as emulsifier in the preparation of wax coatings for fruits and vegetables to help them last longer and remain fresh even during prolonged transit. Morpholine oleate is added to wax as it enables spreading wax in water based liquid for use as a protective coating to prevent contamination by pests and diseases. Morpholine alone does not appear to pose a health concern because morpholine itself is neither a carcinogen nor a teratogen and does not cause chronic toxicity. However, it is a precursor for potent carcinogenic nitrosamines.

Keywords: Carcinogen, Emulsifier, Morpholine, Teratogen, Wax Coating

I. INTRODUCTION

The practice of fruit/vegetable coating was accepted long before their associated chemistries were understood, and are still practiced till date. The first wax coating was applied to citrus fruits in 12th-13th centuries in China. Today, it has expanded rapidly for retaining quality of a wide variety of foods/vegetables, with total annual revenue exceeding $100 million [1]. Currently coatings are widely used on whole fruits to reduce water loss, improve appearance by imparting sheen to the fruits’ surface for aesthetic purposes, provide a carrier for fungicides or growth regulators and create a barrier to gas exchange between the commodity and external atmosphere. Waxing process reduces air permeability of the peel, avoiding the rapid oxidation of fruits and vegetables [2]. Use of wax has become essential when the shelf life of food must be extended, especially when transport for long distances. Nevertheless, for many kinds of food, coating continues to be one of the most cost effective ways to maintain their quality and safety. Different commercial available waxing is used in fruits and vegetables for different roles and applications as summarized in table 1.

Table 1
Commercial available fruits/vegetables coating

<table>
<thead>
<tr>
<th>Commercial Name</th>
<th>Chemical Component</th>
<th>Uses</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshseel</td>
<td>Sucrose esters</td>
<td>Extending shelf life of melon</td>
<td></td>
</tr>
<tr>
<td>Fry shield</td>
<td>Calcium pectinate</td>
<td>Reduces fat uptake during frying fish, potatoes and other vegetables</td>
<td></td>
</tr>
<tr>
<td>Nature seal</td>
<td>Calcium ascorbate</td>
<td>Apples, avocado, carrot and other vegetables</td>
<td></td>
</tr>
<tr>
<td>Nutrasave</td>
<td>N.O-Carboxymethyl chitosan</td>
<td>Reduces loss of water in avocado retains firmness</td>
<td></td>
</tr>
<tr>
<td>Opta Glaze</td>
<td>Wheat gluten</td>
<td>Replaces raw egg based coating to prevent microbial growth</td>
<td>[3]</td>
</tr>
<tr>
<td>Seal gum, Spray gum</td>
<td>Calcium acetate</td>
<td>Prevents darkening of potato during frying</td>
<td></td>
</tr>
<tr>
<td>Semperfresh</td>
<td>Sucrose esters</td>
<td>Protect pome fruits from losing water and discoloration</td>
<td></td>
</tr>
<tr>
<td>Z Coat</td>
<td>Corn Protein</td>
<td>Extends shelf-life of nut meats, pecan &amp; chocolate covered peanut</td>
<td></td>
</tr>
<tr>
<td>PrimaFresh, Shield-Brite Natural Shine</td>
<td>Wax (Esters)</td>
<td>Prevents dehydration and weight loss during transit and Maintains fruit firmness and pressure</td>
<td>[4]</td>
</tr>
<tr>
<td>Carnauba wax Emulsifier with morpholine or other amines</td>
<td>alpha-hydroxy esters and cinnamic aliphatic diesters</td>
<td>Gloss and durability candy coating and coating for nuts, fruits and vegetables</td>
<td>[5,6,7]</td>
</tr>
</tbody>
</table>

II. MORPHOLINE AS GLAZING AGENT: GLOBAL SCENARIO

Consumers around the globe demand for food of high-quality and extended shelf life with anti-microbial properties. Many storage techniques have been developed to extend the marketing distances and holding periods for commodities after harvest. For this, different preservation methodologies have been developed for fruits and vegetables. One such method is coating or edible coating.
with glazing agent. Normally liquid wax spray is used as a protective coating on fruit and vegetables to reduce moisture loss and thereby extend the shelf-life of the product. By nature, many fruits and vegetables make their own natural protective waxy coating to help retain moisture but this protective layer wears off after being cleaned for the packing procedure. In order to overcome this, morpholine is added in the form of a wax like substances as morpholine oleate because it dissolves well and hence can be applied evenly as water based liquid. Once the layer present on the fruits gets dried by hot air treatment, any residual morpholine evaporates and only trace levels are left behind. An important feature is that, heterocyclic ring nucleus of morpholine or its derivatives play an important role in antimicrobial activity [8, 9, 10, 11] and so help fruits and vegetables last longer and remain fresh during prolong transit by preventing them from getting contamination by microbes and diseases to offer cost saving solutions to both farmers and consumers. Other feature is that morpholine has higher permeability to oxygen and water vapor due to less volatility and thus stays longer in the coating. It’s high solubility in water and strong alkaline properties make morpholine a carrier for brightener. Due to these facts, globally, morpholine is used as emulsifier to wax fruits and vegetables and as a carrier for glazing agents. However in the presence of excess nitrite, formed mainly from naturally-occurring nitrate in the diet, morpholine can be chemically nitrosated to form N-nitrosomorpholine (NMOR) a potential carcinogen. Formation of NMOR is well known in aqueous solutions of nitrite or by reaction of gaseous nitrogen oxides, e.g., N₂O₃, N₂O₅, NOₓ in aqueous solutions even under normal environmental conditions [12, 13, 14, 15]. The reaction is summarized as described by Mirvish, 1975, 1988 [12, 13] in figure 1 shown below:

![Fig 1: Formation of NMOR by nitrosation of morpholine](Image)

Now a days, morpholine is used to coat fruits and vegetables such as apples, avocados, bell peppers, cantalopes, cucumbers, eggplants, grapefruits, lemons, limes, melons, oranges, parsnips, passion fruit, peaches, pineapples, pears, pumpkins, rutabagas, squash, sweet potatoes, tomatoes, turnips, almonds and yucca. Morpholine, an ingredient used as an emulsifier in fruit wax formulations, is approved for use in most major apple-producing countries. This practice is widely used in USA, Canada, Mexico, Chile, South Africa, Australia, Japan and other parts of the world [16]. Most of the fruit and vegetable coatings manufactured in the United States contain morpholine oleate, because of its excellent emulsifying and plasticizing properties. However, no evidence has been made in the European Community to approve this additive. Therefore, the use of these carriers is referable on fruit and vegetable coating, leading to food adulteration. Where the Coatings are regulated by US FDA and other regulatory agencies globally, it is approved as “Generally Recognized as Safe (GRAS)” for human consumption. The amount of commercial coatings applied to fruit is negligible, approximately 0.2ml (1 drop) of wax per piece of fruit, as approved by some regulatory agencies but a more comprehensive risk-assessment study is necessary to know if NMOR is accumulated in long term after consumption of coated fruits. In October 2010, UK Food Standards Agency had undertaken an initial risk-assessment of morpholine coated fruits/vegetables and found that morpholine at the levels detected, 0.03-0.3ppm, is likely to be of a low risk to consumer health. Therefore the use of morpholine is prohibited in United Kingdom (UK) and European Union (EU) and countries where its use is permitted are fully aware of these restrictions allowing strict protocol limits of 0.03-0.3 ppm. Morpholine is not permitted in Europe because of a precursor of carcinogen NMOR. So, UK Food standards agency banned the import of apple from Chile because it was found to have about 2ppm of morpholine and advised that affected apples should not be on sale in the UK. Good Fruit Grower, www.goodfruit.com/eu-regulations-stifle-fruit.exports [17] Kolberg et al., 2012 [18] reported the presence of different amines including morpholine in coated fruits/vegetables in order to disperse the wax and to facilitate its application. In their studies (table 2 and figure 2), a total number of 256 samples of fruit were analyzed for morpholine, diethanolamine and triethanolamine using QuPPE method from October 2010 to May 2012 and 33 (14.1 %) of the samples tested positive for at least one of the residue of these three compounds [19].

<table>
<thead>
<tr>
<th>Different Amines</th>
<th>No of Positive samples</th>
<th>Conc. of available amines (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethanolamine</td>
<td>14</td>
<td>0.012-5.3</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>13</td>
<td>0.016-0.37</td>
</tr>
<tr>
<td>Morpholine</td>
<td>16</td>
<td>0.047-25.3</td>
</tr>
</tbody>
</table>
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Fig. 2: Different concentration of amines used in fruits coating

So, European Food Safety Authority (FSA) is indeed preparing a risk assessment document to ascertain whether there is an issue with the unapproved use of morpholine on apples and other products imported into UK. However there is no food additive guideline for morpholine in India and other Asian countries.

III. PRELIMINARY STUDIES FROM INDIA

Pilot studies conducted by us also indicate presence of morpholine in some fruits and vegetables purchased from local super market in Hyderabad, India. There are different analytical methods of estimation of morpholine [20, 21, 22, 23]. In the present study, the average concentration (in duplicate) of morpholine was estimated in these fruits and vegetables; 0.171 mg/kg of tomato, 1.831 mg/kg of carrot and 0.342 mg/kg of capsicum as per spectrophotometric method [24, 25] as shown in figure 3. Although the amounts of morpholine in these fruits and vegetables are below the acceptable range of 0.48 mg/kg body weight/day [26], it does not rule out the risk of formation of NMOR if consumed directly and continuously. Considering the fact that formation of NMOR may lead to cancer over a period of time it is certainly not a situation to be ignored.

Fig. 3: Presence of morpholine in some fruit and vegetable, Hyderabad, India

IV. CONCLUSION

Almost every fruit/vegetable available in modern supermarket contains chemicals that are not natural. It is well known that fresh fruits and vegetables are transported over long distances and a coating is applied post-harvest using glazing agents to shield their surfaces from insects and fungi. Morpholine is one of the common glazing agents and has an inherent tendency to oxidize to nitroso
compounds which are known carcinogens. Given the growing emphasis on increasing the intake of vegetables/fruits to fight the global epidemic of obesity even trace amount of glazing agent/s can be dangerous. In our preliminary study, although morpholine concentration was found to be relatively low and within Acceptable Daily Intake (ADI) but accumulation of NMOR by daily intake of coated fruits/vegetables is a serious threat to health and in the long term, impacting the quality of life. In order to overcome this problem, we strongly suggest the mantra of 3W (Wipe, Wash and Soak in Water for a longer time) and also caution that consumers should not fall prey to bright and dark color of fruits and vegetables. Preferences for local and seasonal product may actually be a healthier choice as this may not be subjected to synthetic coating as no long transits are required from point of cultivation to point of consumption in the producer-consumer chain. Since fruits and vegetables pass through multiple hands from farm to reach our plate, ensuring their safety require good farming practices (GFP), good storage, transportation, retail and restaurant practices to make our food worthy of consumption. Let all authorities work together to make our fruits and vegetables safe by investing in developing a natural product based coatings, based on Aloe vera gel, Chitosan, etc., which are safe (amine free) and harmless to the environment too- as “a green alternative” to synthetic coating.

**REFERENCE**

[20] Dawei Chen, Hong Miao, Jianhong Zou, Pei Cao, Ning Ma, Yunfeng Zhao, Yongning QuPPE method published by the EURL-ESV.