

# PERFUMER & FLAVORIST

## The Oxidative Stability and Retention of a Limonene-Based Model Flavor Plated on Amorphous Silica and Other Selected Carriers\*

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**M**ost flavor chemicals are liquids; however, many food products require that the flavor is in a dry free-flowing form. For example, a dry flavor is necessary in situations where a flavor is to be incorporated into gelatins, dry beverage mixes and dry cake and cookie mixes. The simplest means of producing a dry flavor is to "extend" or "plate" a liquid flavor on a dry edible carrier.

In the typical manufacturing process, the carrier is first added to a mixer (or blender) and the mixer is turned on to fluidize the carrier. The liquid flavor is then sprayed onto the carrier until the desired amount of flavor has been applied.

The only equipment required for this process is a mixer (preferably closed) which is capable of fluidizing the carrier and also has a spray applicator that can uniformly distribute the liquid flavoring.

Several types of closed mixers can be used to produce plated flavors. Three examples include: (1) a liquids/solids V-blender with an intensifier bar; (2) a Littleford Mixer with intensifier blades;\* and (3) a Stephan Mixer.\*\*

If the flavoring is viscous, such as are many spice oleoresins, auxiliary pumps and heaters may be needed to facilitate the plating of the flavor onto the carrier.

The liquid flavor can be plated on many different types of carriers. The carrier must be approved for food use and must be compatible with the flavor and the end product.

The traditional and most commonly used flavor carriers are salt (sodium chloride), simple sugars (lactose, sucrose and glucose) and hydrolyzed starches (maltodextrins).

\* Littleford Brothers, Florence, KY

\*\* Stephan Machinery, Columbus, OH

\* Peer reviewed

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The patent literature reveals that flavors are plated onto just about anything that is considered edible. Tea and coffee solids, sweet whey, dry milk, cracker meal, cereal solids, vegetable pulp, insoluble fibrous alginates, spent bran and wheat flour are examples of carriers that have been used. Specialty products, such as microporous starches<sup>1,2</sup> and amorphous silicas<sup>3-9</sup> are also cited in the patent literature as flavor carriers.

Little information is published regarding the effect of the carrier on the plated flavor. It is empirically recognized that flavors plated on salt and sugars rapidly oxidize and are readily lost due to evaporation. In addition, the maximum amount of flavor that can be applied to salt and sugars is low, ranging between 3 and 7%.

The use of modified starches as flavor carriers offers increased flavor-loading capacities. Spray-dried maltodextrins, which are commonly used to carry liquid flavors, can hold up to 25% of their weight in flavor before they become tacky. However, like the sugars and salt, flavor loss occurs rapidly by evaporation and the flavor is afforded no protection against oxidation.

A product brochure published by a manufacturer of specialty maltodextrins\* proposes that the applied flavor loads by simple plating can be increased up to 3:1 (weight of flavor to carrier) for light flavor oils and up to 1:1 for viscous oils by using their agglomerated porous maltodextrin\*\* product.<sup>10,11</sup> It is not known whether this type of product restricts volatile flavor loss or offers any oxidative protection to an applied flavor.

Also absent from the scientific literature is information regarding the use of amorphous silicas to carry flavors. In the United States amorphous silicas have GRAS status and are approved for use as flavor carriers with limitations. The use of amorphous silica cannot exceed 2% by weight in the final food and currently can only be used to "encapsulate" lemon oil, distilled lime oil, orange oil, peppermint oil and spearmint oil (21CFR 172.230 and 21CFR 172.480).

In 1986, Villota and Hawkes reviewed the food applications and health implications of handling and ingesting amorphous silicon dioxide. The authors acknowledged that scientific literature on the flavor-retaining properties of amorphous silica is scarce.<sup>12</sup>

We learned of the use of amorphous silicas as flavor carriers from the late Dr. Paul Perry. Dr. Perry stated (personal communication, University of Minnesota Flavor Applications Short Course, 1988) that high flavor loads (2:1) were obtainable with amorphous silica and that a flavor would not deteriorate or be lost as quickly when plated on amorphous silica as with traditional carriers. A subsequent search into the patent literature revealed that the food and flavor industry has been using amorphous silicas as flavor carriers for many years.

We found that a patent was granted to the Pillsbury Co. (1968) for the use of amorphous silica to carry an edible

flavor oil.<sup>3</sup> The silica also functioned as a flavor release agent in the finished product. Another U.S. patent (1970) cited the use of fumed amorphous silica as a carrier for liquid spice extracts.<sup>4</sup>

International Flavors & Fragrances Inc. was granted a patent (1975) which described the use of colloidal amorphous silica to carry a hydrophobic flavor oil.<sup>6</sup> The flavored silica was subsequently mixed with an encapsulated flavor oil and this combined flavor system provided sustained release of flavor in a chewing gum application.

In 1977, a Danish patent described the plating of an ethanol-based alcoholic beverage flavor (1 part flavor:1 part carrier) onto amorphous silica.<sup>7</sup>

More recently, a German Patent (1989) described a process for the manufacturing of a ground roast coffee with improved flavor and storage stability. The cooled roasted coffee was mixed with an adsorbent silica (up to 15% by weight). During further processing, the silica was said to adsorb, retain and stabilize the coffee aromas that were formerly lost during the grinding process.<sup>9</sup> These five patents are just a sample of the applications that incorpo-

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\* A. E. Staley Manufacturing Co., Decatur, IL

\*\* Micropor Buds 1015A



## Oxidative Stability and Retention

**Table I. Physical and chemical properties of the commercial silicas**

Analysis*	Sylox 15	Syloid 74	Syloid 244
<b>Physical properties</b>			
Particle size ( $\mu$ )			
Coulter 70 $\mu$ aperture	4.1	6.7	3.9
Malvern	8.4	7.7	6.6
Surface area (m <sup>2</sup> /g)	209	302	434
Hg Poresimeter			
Pore volume (cc/g)	2.0-2.5	1.2	1.6
N <sub>2</sub> Adsorption			
<b>Chemical properties (% Dry Basis)</b>			
Al <sub>2</sub> O <sub>3</sub>	0.12	0.04	0.05
Na <sub>2</sub> O	0.69	0.06	0.05
CaO	0.07	0.14	0.10
MgO	0.03	0.04	0.03
Fe <sub>2</sub> O <sub>3</sub>	0.03	0.01	0.01
SO <sub>4</sub>	0.18	0.06	0.04
SiO <sub>2</sub>	98.84	99.61	99.67
Loss on drying 145°C	10.54	4.06	11.64
pH (5% slurry)	8.97	7.34	7.87

\* Data courtesy of W. R. Grace & Co., Davison Technical Center, Baltimore, MD 1990

**Table II. Molecular weights and boiling points of flavor compounds**

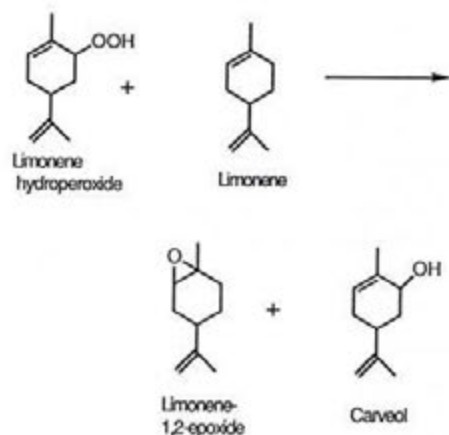
Compound	Molecular wt.	Boiling pt.°C
acetaldehyde	44.05	21.0
ethyl acetate	88.11	76.5
thiophene	84.14	84.2
ethyl propionate	102.13	99.0
ethyl butyrate	116.16	120.0
2-hexanone	100.16	127.0
2-methyl pyrazine	94.12	135.0
heptaldehyde	114.19	153.0
2-octanone	128.22	173.0
limonene	136.24	175.5
benzaldehyde	106.12	178.5
cinnamic aldehyde	132.16	253.0
eugenol	164.20	254.0

**Table III. Percent (g flavor/g total) of model flavor plated on each carrier**

Carrier	% Flavor	Carrier	% Flavor
sucrose	3	M100	3, 10, 20
D-fructose	3	Micropor Buds 1015A	3, 10, 20
D-glucose	3	Syloid 74	20, 50
D-lactose	3	Syloid 244	20, 50
NaCl	3	Sylox 15	20, 50, 66.7
cantab	3		



**Figure 1. Decomposition of limonene hydroperoxide to carvone**



**Figure 2. Decomposition of limonene hydroperoxide to 1,2-limonene epoxide and carveol**

rate the use of silica as a flavor carrier.

The above mentioned patents clearly establish that amorphous silicas are currently being used as flavor carriers and that the use of amorphous silicas as flavor carriers is not a new idea. It is of interest that information on the use of amorphous silica as a flavor carrier (i.e., flavor-loading capacity, flavor retention and the stability of a flavor plated on silica) is absent from the scientific literature.

The objective of the following study was to evaluate amorphous silica for use as a flavor carrier. Our study was limited to two different types of amorphous silicas, specifically two aerogels and one xerogel. In order to compare the performance of these silicas to other flavor carriers, a selection of traditional carriers (sodium chloride, dextrose, fructose, glucose, lactose and sucrose) as well as newer materials\* was included in this study.

### Experimental Details

**Selected Carriers**—The carriers evaluated in this study were (all of the carriers were used as received):

**sucrose** (granulated cane sugar, California and Hawaiian Sugar Co., Concord, CA), **D-fructose** (98% pure crystalline, Aldrich, Milwaukee, WI), **D-glucose** (anhydrous granular, Spectrum Chemical Manufacturing Corp.,

\* Maltodextrin and Micropor Buds 1015A

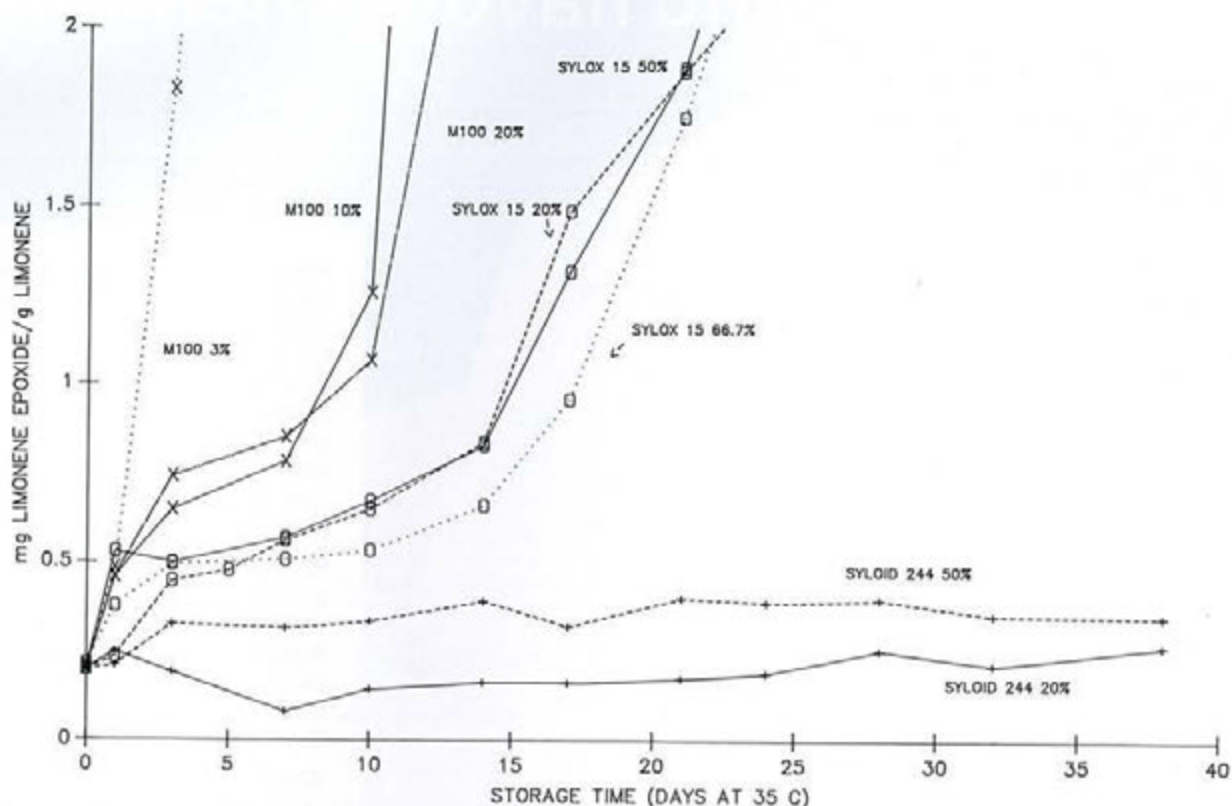


Figure 3. Shelf-life of model flavor plated on M100, Sylox 15 and Syloid 244

Redondo Beach, CA), **D-lactose** (monohydrate powder, J.T. Baker, Phillipsburg, NJ), **Sodium chloride** (NaCl, USP table crystal, Morton Salt, Chicago, IL), **Cantab** (an agglomerated glucose, Penford Products Co., Cedar Rapids, IA), **M100** (a 10DE spray dried maltodextrin, Grain Processing Corp., Muscatine, IA), **Micropor Buds 1015A** (a specialty processed agglomerated 10DE maltodextrin, A. E. Staley Manufacturing Co., Decatur, IL), **Syloid 74** (an amorphous silica xerogel, W. R. Grace & Co., Baltimore, MD), and **Sylox 15** and **Syloid 244** (both amorphous silica aerogels, W. R. Grace & Co., Baltimore, MD).

The physical and chemical characteristics of the silicas evaluated in this study are presented in Table I. Sylox 15 and Syloid 74 and 244 are silica gels which have completely hydroxylated surfaces.<sup>13</sup>

**Model Flavor**—A limonene-based model flavor was prepared using 88% D-limonene and 1% of each of the following flavor compounds: acetaldehyde, ethyl acetate, thiophene, ethyl propionate, 2-hexanone, ethyl butyrate, 2-methyl pyrazine, heptaldehyde, benzaldehyde, 2-octanone, cinnamic aldehyde and eugenol. All of the flavor compounds were supplied by Aldrich Flavors and Fragrances (Milwaukee, WI). Table II contains the relevant physical data on these flavor compounds.

**Sample Preparation**—The carriers and percent compositions of model flavor plated onto each of the carriers are presented in Table III. All of the samples were prepared in 200.0 g batches.

The plating procedure was accomplished by first adding the appropriate amount (6.0-133.3 g) of model flavor into a separatory funnel. The carrier (194.0-66.7 g) was weighed into a ca. 500 mL rounded glass mixing bowl. The separatory funnel was positioned such that the tip of the funnel rested on the top inside lip of the bowl. The separatory funnel stopcock was then opened to permit drop-wise addition of the flavor down the side of the bowl and onto the carrier.

The flavor was blended with the carrier by hand using a stainless steel whisk and spatula. Blend time was kept at a minimum but varied depending on the type of carrier and the amount of applied flavor. The salt and carbohydrate carriers required minimal blending (3-5 minutes).

Special care was taken when blending the Micropor Buds 1015A and the Cantab products to maintain the integrity of the agglomerated structure. Mixing of these two carriers with the flavor was only performed with the whisk. The silica carriers required more blending (5-8 minutes) to evenly distribute the flavor.

**Sample Storage**—Samples (10.00 g) of each carrier/flavor combination were weighed into vials and duplicate



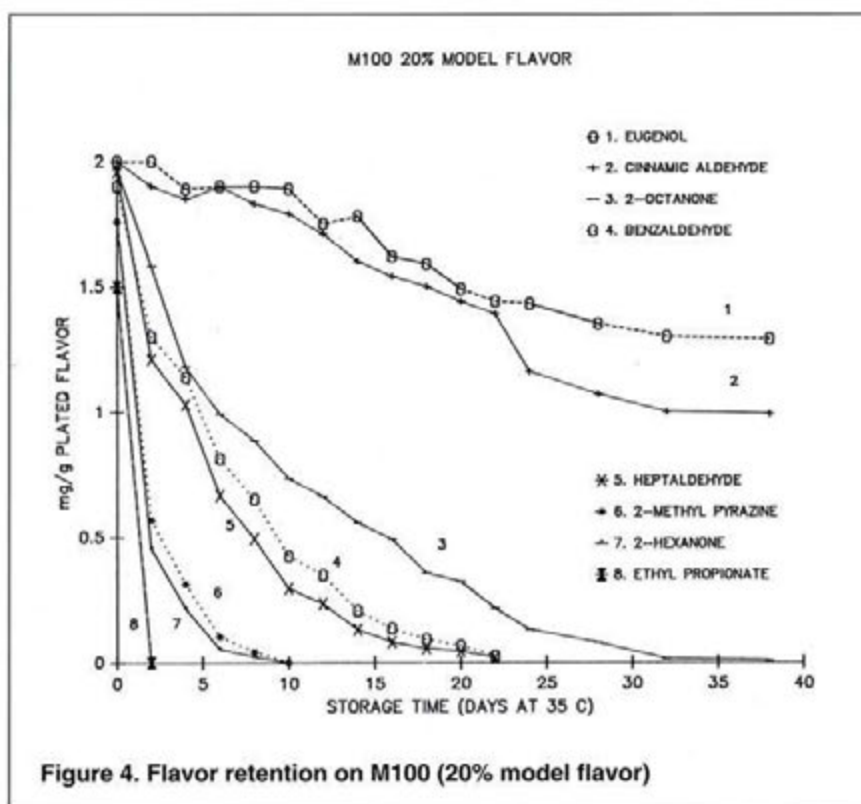


Figure 4. Flavor retention on M100 (20% model flavor)

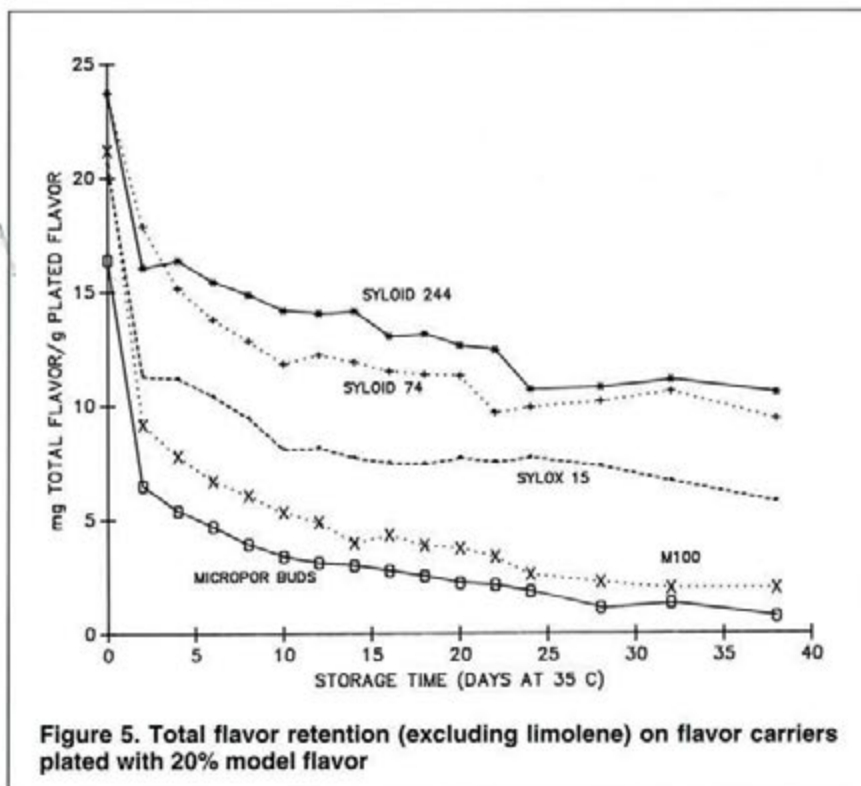


Figure 5. Total flavor retention (excluding limonene) on flavor carriers plated with 20% model flavor

sets (20 per set) of each carrier/ flavor were used in the study. For one of the two sets of samples, the vial caps were left off in order to monitor flavor loss. The second set of vials was capped to enable monitoring flavor oxidation independently of flavor loss. The samples were placed in a 35°C

incubator and 10-15% relative humidity. Samples were taken for analyses initially (just after plating) and then every 2-3 days.

**Analyses**—The amount (g flavor/g carrier) of each flavor compound remaining on the carrier and the oxidation products of limonene were determined by capillary GC.

For the storage studies, the model flavor was first recovered from the carrier by extracting the carrier with 20 mL of an acetone standard solution (0.1 mg/ml of tridecane was added to the acetone as an internal standard). The acetone was added directly to the sample vial. The vial was capped and then vortexed for 1 min. The carrier was allowed time to settle out of solution (ca. 2-4 hrs at 4°C). An aliquot of the acetone extract was taken from the top of the sample vial and a direct liquid injection (1-2  $\mu$ L with a 1:40 split) of the extract was made into a GC.

The flavor compounds were separated using a Hewlett Packard 5890 Series II Gas Chromatograph and a DB-5 column (30 meters, 0.32 mm inside diameter, 1  $\mu$  film thickness, J & W Scientific, Rancho Cordoba, CA). The following GC run parameters were used: initial oven temperature 40°C, initial time 2 min, oven program rate 5°C/min, and final oven temperature 250°C.

An internal standard procedure was used to determine the amount of each flavor retained on each sample as well as the quantities of known limonene oxidation products (limonene epoxide, carvone and carveol) formed during storage.

Preliminary studies demonstrated that 97-104% of all the compounds added to the model flavor were recovered by the acetone extraction. In addition, limonene epoxide, carvone and carveol were recovered equally well by this procedure.

Static headspace analysis was also carried out on all of the samples just after plating. Headspace sampling was accomplished using a Hewlett Packard 19395A Automated Headspace Sampler. Samples (1.0 g) were weighed into 20 mL glass headspace vials. The sample vials were capped and sealed with Teflon lined septa and equilibrated at 35°C for 2 hrs. An injection program with a 15s vial pressurization, a 15s vent (3 mL loop) and 90s injection onto the GC was used.

The sample injection was cryo-focused by inserting the

Table IV. Physical properties of the three silicas

Silica	Total pore volume cc/g	Total pore <sup>1</sup> diameter (Å)	Total surface area of pore openings (Å <sup>2</sup> )	Total % pore vol. filled		
				20%*	50%	66.7%
Sylox 15	2.3	431	1.46 x 10 <sup>5</sup>	10	48	90
Syloid 74	1.2	159	1.99 x 10 <sup>4</sup>	22	85	
Syloid 244	1.6	147	1.70 x 10 <sup>4</sup>	16	63	

1. Pores were assumed to be cylinders. Average total pore diameter/g was estimated from the average total pore volume cc/g and average total surface area m<sup>2</sup>/g: Average total pore diameter Å/g = (4 x pore volume cm<sup>3</sup>/surface area m<sup>2</sup> x 10<sup>4</sup> cm<sup>2</sup>/m<sup>2</sup>) x 10<sup>8</sup> Å/cm.

2. A density of 0.84 g/cc (density of limonene) was assumed for the model flavor. Flavor lost during plating (Table V) is accounted for in the values reported for % pore volume filled.

\* flavor load

Table V. Percent of total flavor lost during plating and storage (excluding limonene)

Carrier	Percent total flavor loss					
	0 <sup>1</sup>	2	8	12	20	38
<b>3% Model Flavor</b>						
NaCl	54	73	91	99	*	*
sucrose	50	75	93	99	*	*
fructose	46	80	92	99	*	*
lactose	57	79	94	*	*	*
dextrose	49	77	92	99	*	*
cantab	53	82	89	99	*	*
M100	61	80	92	99	*	*
Micropor Buds	63	88	98	*	*	*
<b>10% Model flavor</b>						
M100	35	72	82	88	90	94
Micropor Buds	51	66	86	90	92	96
<b>20% Model flavor</b>						
M100	22	57	71	77	81	91
Micropor Buds	40	61	76	81	82	93
Sylox 15	24	42	54	61	63	68
Syloid 74	13	25	46	49	52	55
Syloid 244	15	31	36	39	46	52
<b>50% Model flavor</b>						
Sylox 15	10	60	72	77	82	84
Syloid 74	15	49	58	64	70	75
Syloid 244	15	45	53	58	65	70

<sup>1</sup> Time (days at 35°C)

first ca. 20 cm of the capillary column into liquid nitrogen. Separation was accomplished using the same GC, column and run conditions that were described for the liquid injection.

**End of Shelf-Life**—For this study end of shelf-life was defined as when the amount of limonene epoxide formed during storage exceeded 2.0 mg/g limonene.<sup>14</sup>

## Results and Discussion

**Limonene Oxidation**—The oxidation of limonene results in off flavors which are typically described as "piney," "turpentine-like" or "painty." Many natural flavor oils, primarily citrus oils, are made up of 60-95% limonene. The total worldwide production of citrus oils is approximately 19,590 tons.<sup>15</sup>

Preserving the quality of these flavor oils is of great economic significance. Limonene has been protected against oxidation in citrus oils by spray-drying,<sup>16</sup> extrusion,<sup>17</sup> coacervation and inclusion in β-cyclodextrin.<sup>18</sup>

However, if limonene or flavor oils comprised of limonene are exposed to light and air, limonene readily oxidizes by two known mechanisms: photosensitized oxidation and autoxidation.<sup>19-24</sup>

In the presence of light, photosensitized oxidation of limonene involves the 1,3 addition of singlet oxygen to the endocyclic tri-substituted double bond to form limonene hydroperoxide. Limonene hydroperoxide decomposes to form carvone or the hydroperoxide can attack another limonene molecule at the endocyclic tri-substituted double bond to form both limonene-1,2-epoxide and carveol (Figure 1).<sup>20-24</sup>

Autoxidation of limonene occurs via hydrogen abstraction at the alpha position to the tri-substituted endocyclic double bond to form limonene hydroperoxide. The hydroperoxides readily decompose to form the secondary end products carvone, limonene-1,2-epoxide and carveol (Figure 2).<sup>19</sup>

Limonene-1,2-epoxide has been found to be a useful index for monitoring the stability of limonene. Prior studies have shown that 2.0-4.0 mg limonene-1,2-epoxide per g of limonene correlated well to the detection of unacceptable off flavors in cold pressed orange peel oil by a trained sensory panel.<sup>14</sup> Since orange oil is ca. 94% limonene, the use of limonene-1,2-epoxide as a flavor quality indicator was applied to this study and a value of 2.0 mg limonene-1,2-epoxide per gram of limonene was used to define the end of



## Oxidative Stability and Retention

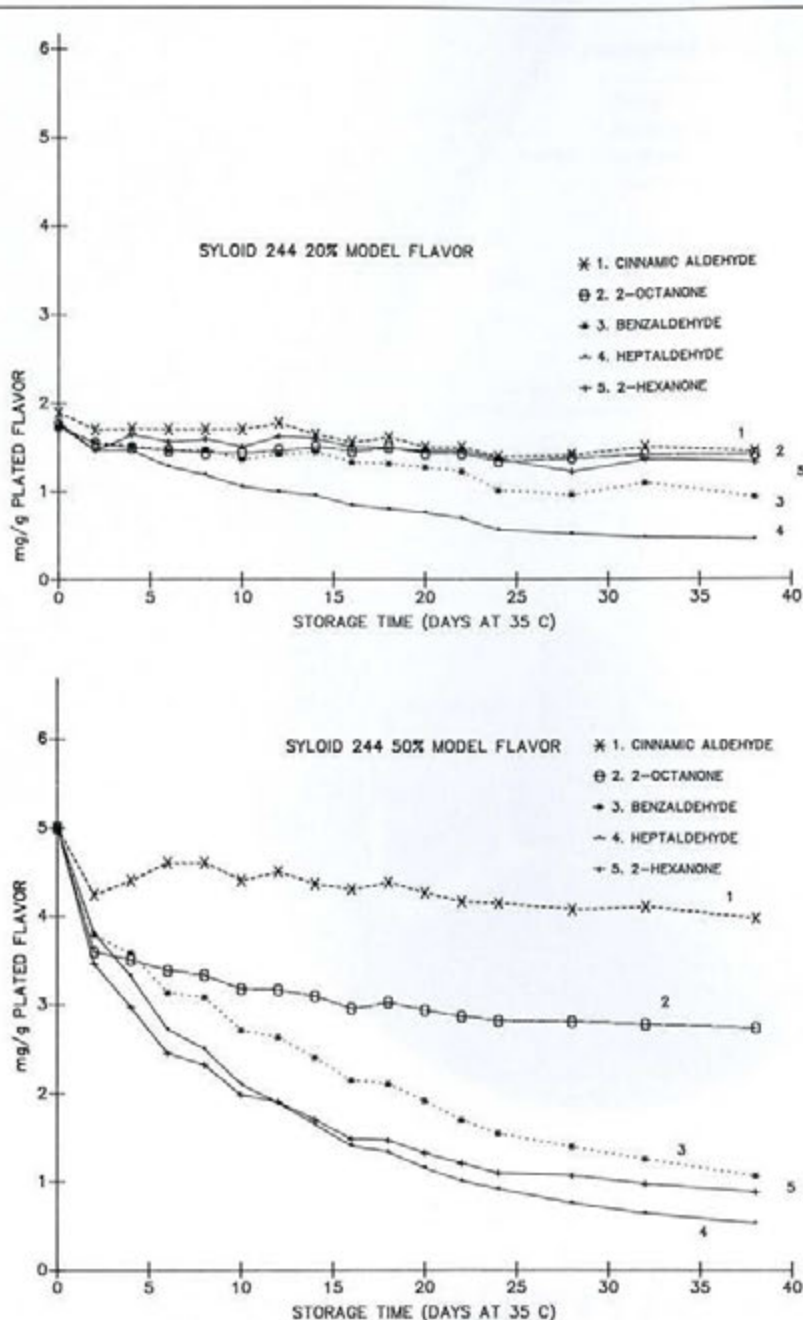


Figure 6a. Flavor retention on Syloid 244 (20% model flavor), b. Flavor retention on Syloid 244 (50% model flavor)

Table VI. Number of SiOH groups compared to the number of adsorbed flavor molecules per gram plated flavor ( $\times 10^{20}$ )

Flavor Load	SiOH groups			Flavor molecules
	Sylox 15	Syloid 74	Syloid 244	
20%	10.1	14.6	21.0	9.0
50%	5.7	8.3	11.9	22.3
66.7%	3.8			27.7

shelf-life for the model flavor.

In the present study, the oxidation of limonene occurred rapidly, within 4-6 days, on all of the carriers plated with 3% model flavor (Cantab, dextrose, fructose, lactose, NaCl, sucrose, M100 and Micropor Buds 1015A). M100 and Micropor Buds 1015A plated at 10 and 20% flavor loads were found to have a shelf-life of 8-10 days.

The model flavor exhibited an extended shelf-life when plated onto amorphous silica compared to the other carriers evaluated in this study. The shelf-life of the model flavor exceeded the time frame of this study (38 days) when plated on Syloid 74 and Syloid 244 at 20 and 50% flavor loads.

A lesser shelf-life (24 days) resulted for the model flavor plated on the Sylox 15 silica independent of the applied flavor load (20, 50 and 66.7% flavor). The shelf-life data for M100, Sylox 15 and Syloid 244 are presented in Figure 3.

The minimal shelf-life (4-10 days) of the model flavor plated on the salt, sugar and carbohydrate carriers is expected. The flavor having been spread thinly on the surface of the carrier is afforded no protection against oxidation. In fact, the rate of limonene oxidation is greatly accelerated as compared to a liquid limonene-based flavoring alone.<sup>14</sup> This occurs because the surface area of the flavor is increased and, as a result, exposure to oxygen is increased.

The extended shelf-life of the model flavor plated on amorphous silica was unexpected. Although scientific literature on the oxidative stability of flavor compounds on amorphous silica is not available, the oxidative stability of vitamins A and E<sup>25</sup> and carthamin (i.e., Natural Red No. 26, saffron)<sup>26</sup> adsorbed in amorphous silica has been the subject of two patents.

The reported stability of these compounds adsorbed in amorphous silica may be relevant to this study. Like limonene, extensive degradation of these compounds occurs in the presence of light or oxygen.<sup>27-30</sup>

In order for silica to protect any molecule against oxidation, the susceptibility of labile bonds to attack by oxygen must be hindered or oxygen must be restricted.

The observed stability of limonene is influenced by differences in the physical and chemical properties of the three silicas evaluated in this study. There are differences in average surface area, average pore volume, average pore diameter, and purity between the three silicas and these

## Oxidative Stability and Retention

differences will change the physical structures and surface chemistries of the silicas (Tables I and IV).

Sylox 15 has a larger pore volume, a smaller total surface area and a larger average pore diameter compared to Syloid 74 and 244. The flavor adsorbed in the Sylox 15 had more area of flavor exposed to air and would be expected to oxidize faster than the flavor adsorbed into the narrower pores of the Syloid 74 and 244 silicas [(average surface area of the pore opening)/(average pore volume) per gram of silica are  $6.4 \times 10^4 \text{ \AA}^2/\text{cc}$  Sylox 15,  $1.7 \times 10^4 \text{ \AA}^2/\text{cc}$  Syloid 74 and  $1.1 \times 10^4 \text{ \AA}^2/\text{cc}$  Syloid 244].

The rate at which limonene becomes oxidized when adsorbed in the silicas would also be expected to depend on the applied flavor load. This would occur because the surface area of the flavor is further increased in a partially filled pore compared to a flavor contained in a completely filled pore. However, the rate at which limonene oxidized when adsorbed in Sylox 15 was independent of the applied flavor load and no new limonene oxidation products were detected after 38 days on the Syloid 74 or 244 silicas irrespective of flavor load (Figure 3).

Another important factor determined by pore size is the density of free hydroxyl groups within each pore. The density of free hydroxyls is greater in narrower pores and a greater density of hydroxyl groups facilitates interactions between the silica surface and adsorbed molecule.<sup>13</sup> Diene bonds (like those present in the limonene molecule) are known to interact with the silica surface through sharing of pi electrons by the oxygen molecule of the silanol group and the carbon-carbon double bond.<sup>13</sup> Limonene may be stabilized by such interactions at monolayer flavor loads (20%) but at higher flavor loads the bulk of the flavor is not in contact with the carrier and such interactions would not occur (see Table VI).

The presence of adsorbed water will prevent limonene from interacting with the silica surface. A fully hydroxylated silica surface has 5-6 silanol (SiOH) per  $\text{nm}^2$ .<sup>13</sup> In the Sylox 15, Syloid 74 and Syloid 244 the proportion of water:SiOH molecules were 3.4:1, 0.85:1 and 1.85:1 respectively (given the surface area and the % moisture of the silicas, Table I). The

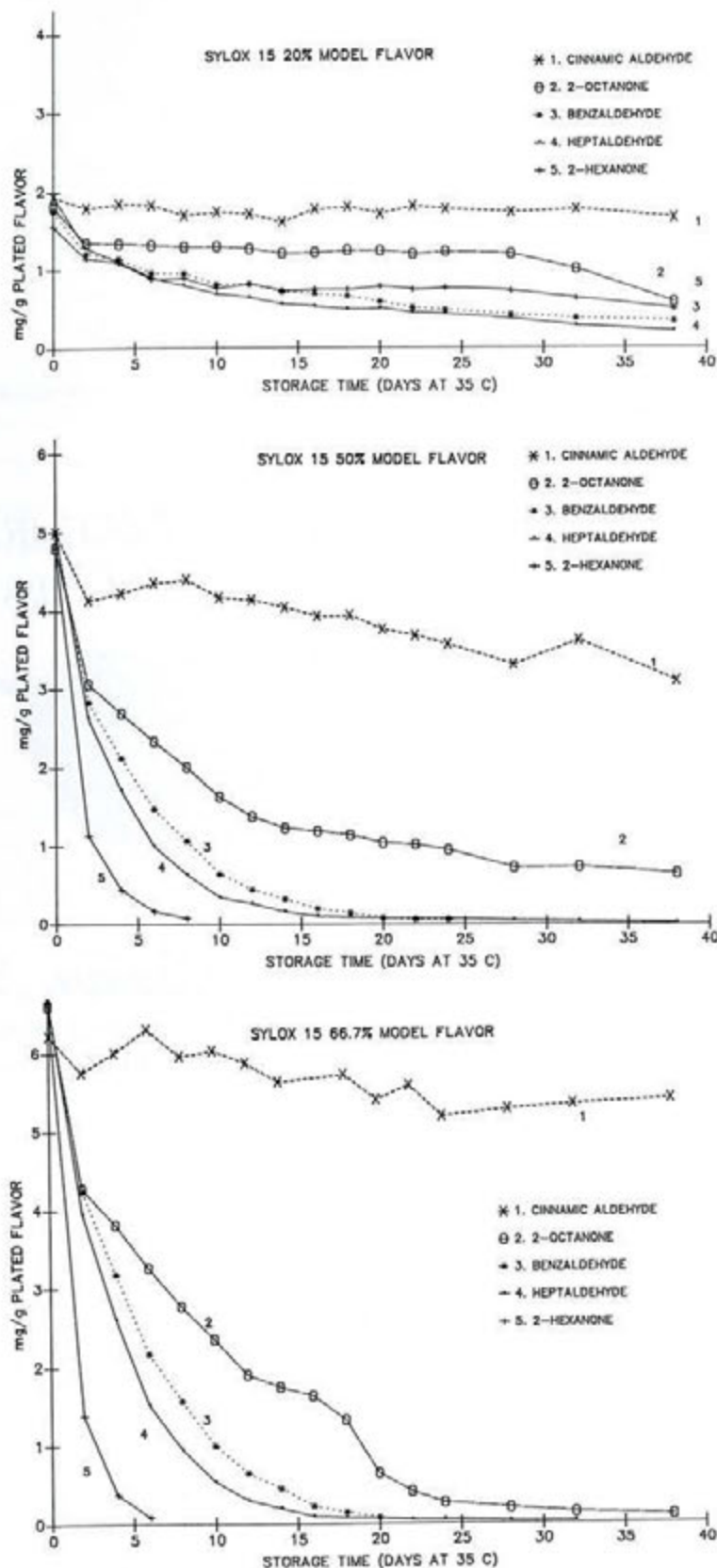


Figure 7a. Flavor retention on Sylox 15 (20% model flavor), b. Flavor retention on Sylox 15 (50% model flavor), c. Flavor retention on Sylox 15 (66.7% model flavor)



adsorbed water molecules are not necessarily distributed equally on the surface of silica. Instead, water can form bi- and tri-layers in localized areas and free silanol groups remain available to interact with other adsorbed molecules.<sup>12,13</sup> It is apparent that Sylox 15 has considerably more surface bound water, but it is not clear how or if this may have influenced limonene oxidation/stability.

Sylox 15 and Syloid 74 and 244 silicas differ in their chemical purity. Normally the presence of trace metals such as iron catalyze the initiation of singlet oxidation of limonene. Concentrations of 10-55 ppm of iron in orange peel oil will produce a catalytic effect.<sup>14</sup> The amount of iron present in all three silicas studied exceeds these concentrations (Table I). However, the iron present in the silica is contained in the bulk of the matrix and would not be at the surface to participate in the oxidation reaction.<sup>13</sup> The silicas contain other impurities (sodium, calcium and magnesium, Table I), but their possible influence on limonene oxidation/stability is not known.

Also discussed in the literature is the ability of a silica gel surface to quench singlet oxidation.<sup>31</sup> Silica gel (Davisil 150 Å pore size) was found to reduce the lifetime of singlet molecular oxygen by ca. 50% compared to the lifetime observed for singlet molecular oxygen in cyclohexane (from 24 μs to 13.4 μs). The observed quenching effect was found to be directly related to the number of isolated free silanol groups on the silica surface. The isolated free silanol groups acted as antioxidants against photosensitized oxidation by quenching singlet molecular oxygen.<sup>31</sup>

The effect of pore size on the quenching of excited aromatic molecules adsorbed on silica has also been investigated.<sup>32</sup> An increase in quenching efficiency was observed as the average pore volume decreased and the total surface area of the particle increased. Smaller pores preferentially adsorbed oxygen and excited organic molecules. The increased quenching effect resulted from an increased concentration of excited molecules

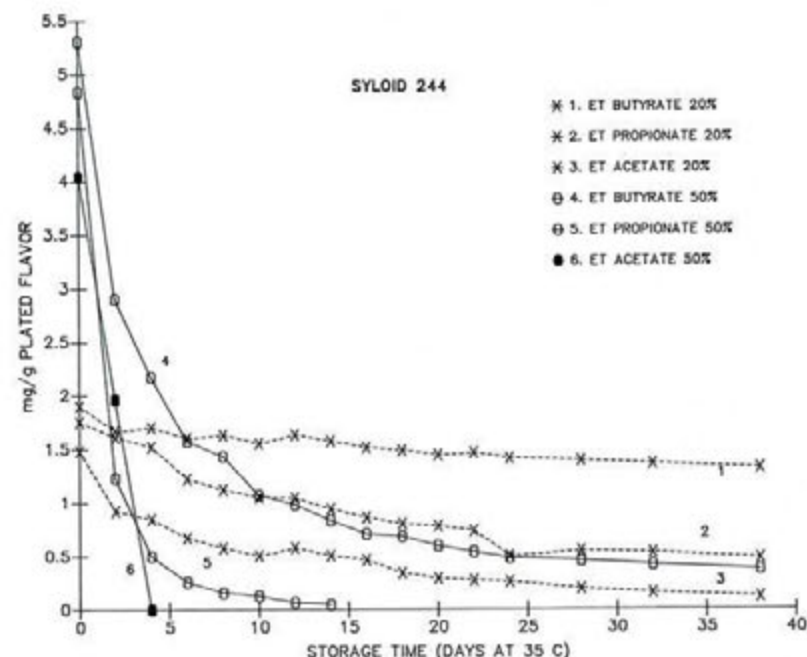


Figure 8. Retention of esters adsorbed in syloid 244 loaded with 20 and 50% model flavor

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## Oxidative Stability and Retention

adsorbed preferentially on the high surface area narrower pores of the silica gel.<sup>32</sup>

It is apparent that the mechanism(s) responsible for the stability of limonene are varied and complex. Continued research focusing on determining the orientation of limonene on the silica surface, the solubility of molecular oxygen in each silica, and the singlet oxygen quenching effect for the three silicas evaluated in this study may provide insight on the mechanism(s) responsible for limonene stability.

**Flavor Retention**—While plating is a very simple and cost effective means of producing dry free flowing flavors, the process has some inherent weaknesses. One such weakness is the lack of protection against oxidative changes and a second is evaporative losses.

Significant flavor loss occurs during the blending process which is used to distribute the flavor on the carrier and is readily apparent by the strong odor of the flavor in the manufacturing area. If the plated flavor is then topically applied to a food (such as a snack food), the flavor will evaporate into the package headspace. Depending on the packaging material, the flavor may be adsorbed into the package itself or diffuse through it.<sup>33</sup>

In either case the flavor is lost from the food. If the packaging material contains the flavor, the flavor accumulates in the packaging headspace and is released into the room when the consumer opens the package leaving little flavor on the food. The magnitude of flavor loss from plated flavors is evaluated in this study. The percent combined flavor losses of the 12 compounds added to the limonene base at selected storage times are presented in Table V.

**Non-Silica Carriers:** A 46-63% combined flavor loss resulted during the plating process alone for all carriers (NaCl, Cantab, dextrose, fructose, lactose, sucrose, M100 and Micropor Buds 1015A) plated with 3% flavor loads (Table V). Within 6-8 days of storage, 90% of the flavor had evaporated and by 12 days less than 1% of the flavor remained. The total flavor lost during the plating of M100 and Micropor Buds 1015A loaded with 10 and 20% model flavor was 22-51%. Additional losses of 57-72% occurred after 4 days and 80-90% of the flavor was lost by 20 days.

The rate at which a flavor is lost from a carrier would

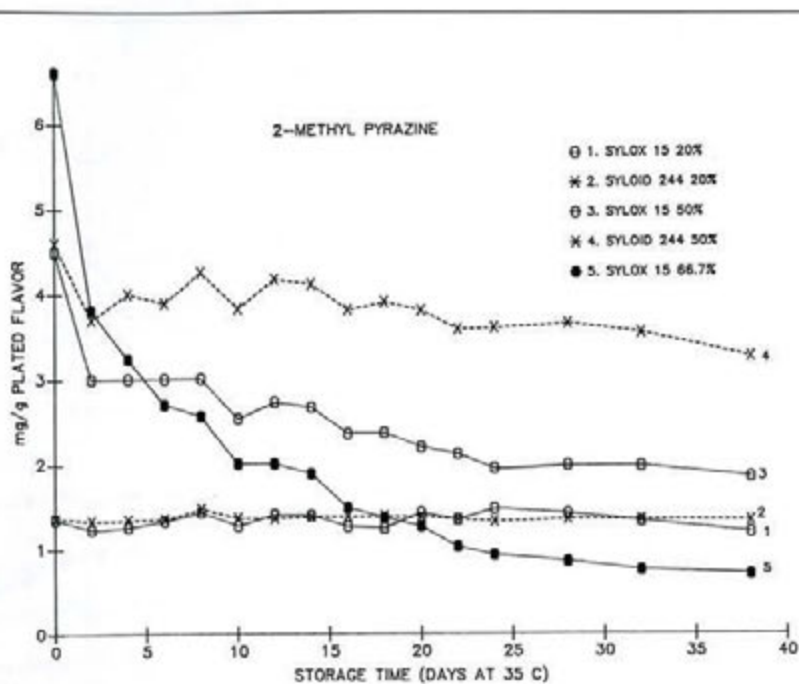


Figure 9. Retention of 2-methyl pyrazine adsorbed in Sylox 15 and Syloid 244 silica at 20, 50 and 66.7% flavor loads

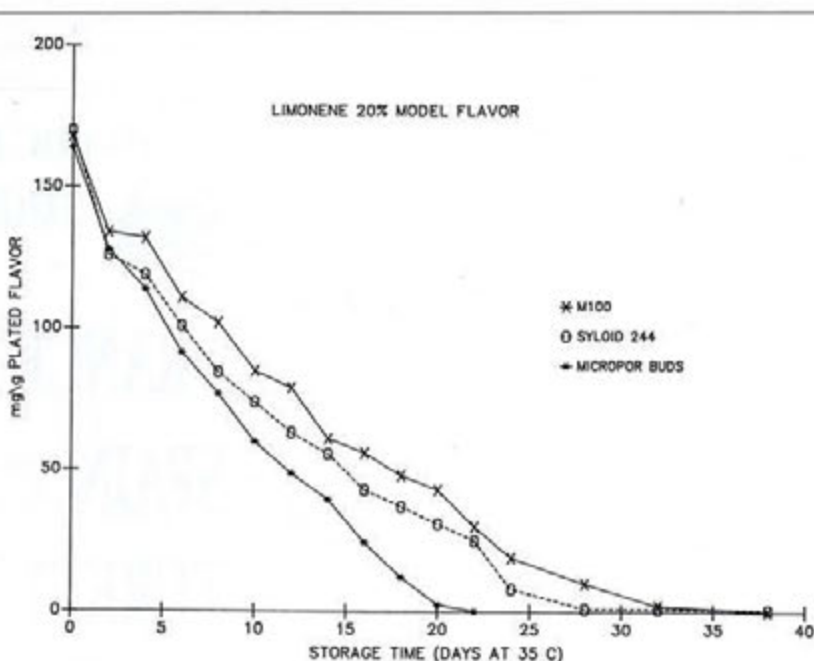


Figure 10. Limonene loss from Micropor Buds 1015A, M100 and Syloid 244 loaded with 20% model flavor

depend on the boiling point of a compound and the ability of the carrier to interact with the flavor molecules. No apparent interaction of flavor and carrier was observed for salt, sugar or carbohydrate carriers. The magnitude of flavor loss from these carriers was dependent only on the boiling point of the individual flavor compounds (Table III). As a



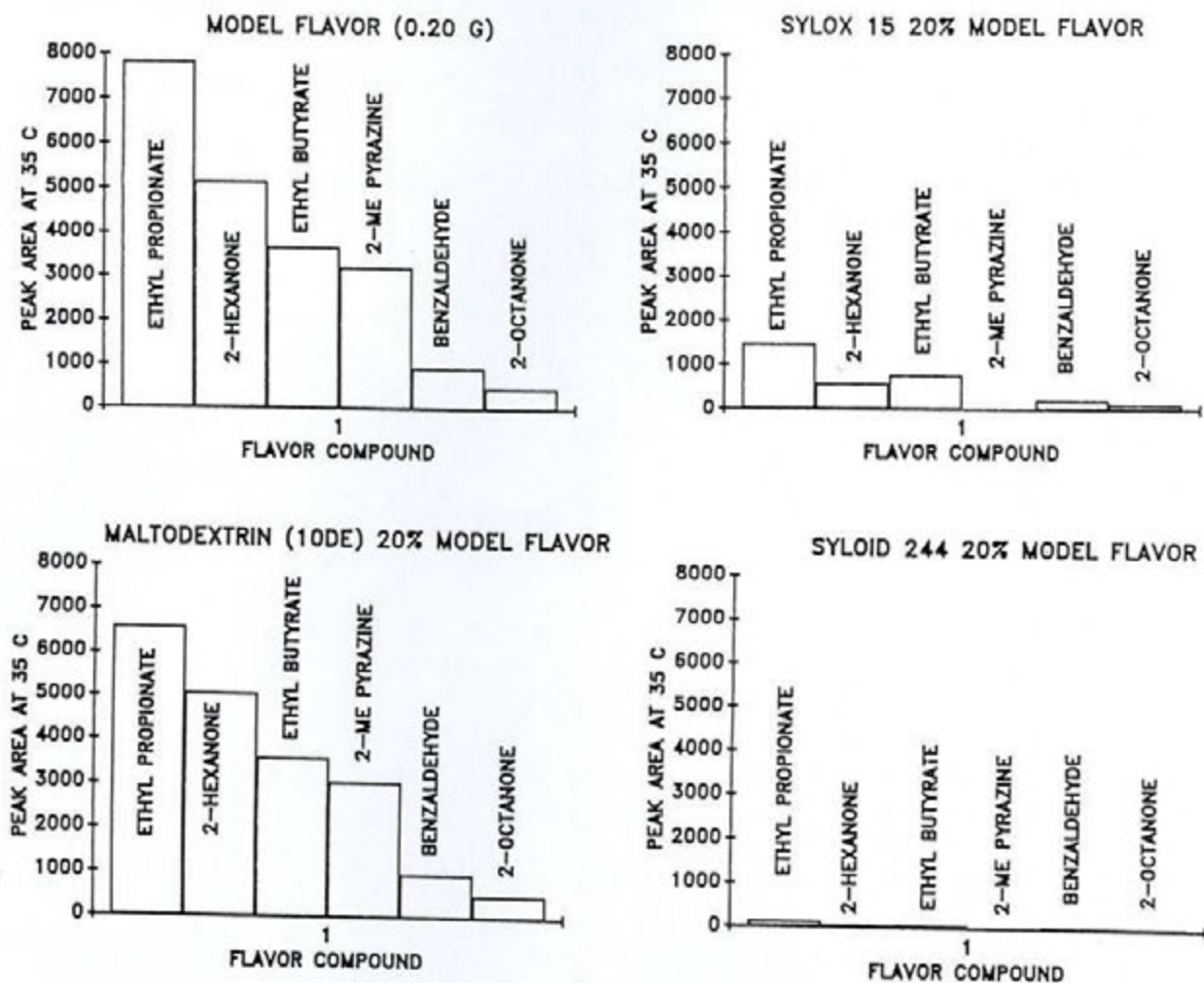


Figure 11. Reduced headspace concentrations of the model flavor absorbed in amorphous silica

result, complete loss of acetaldehyde, ethyl acetate, thiophene and ethyl propionate occurred in two days and compounds with higher boiling points, such as cinnamic aldehyde were retained longer. An example of typical flavor losses represented by M100 is presented in Figure 4.

**Silica Carriers:** The silica products (at 20% flavor loads) demonstrated the ability to retain the model flavor longer compared to M100 and Micropor Buds 1015A (Figure 5). After 38 days of storage, only ca. 55% of the total flavor was lost from the Syloid 74 and 244 silicas, while greater losses occurred on the Sylox 15 (68%).

The increased flavor retention demonstrated by the silicas at 20% flavor loads is due to interactions between the silica surface and the model flavor. On a hydroxylated silica surface, the free silanol groups are primarily where molecular interactions occur.<sup>13</sup> In this study the potential for interactions between an adsorbed compound and the silica surface is optimum at 20% flavor loads (Table VI).

Flavor compounds can interact with the silica surface

differently depending on the chemical properties of the flavor molecule. Hydrogen bond formation between electro-negative atoms of the adsorbed molecule and the hydrogen atoms of the silica silanol group is primarily responsible for the adsorption of organic molecules.<sup>13</sup> Compounds which contain oxygen electron donors, such as ethers, alcohols and ketones, can hydrogen bond with surface hydroxyl groups. The fully hydroxylated surface of the silica gel can more effectively (compared to a partially or fully dehydroxylated silica surface) retain molecules that have multipolar sites that can hydrogen bond to the silica silanol groups.<sup>12,13,34,35</sup> Ionic bonds can also form with the silica surface. The nitrogen of amines and amides and metal salts form strong ionic bonds with the silica gel surface. Hydrophobic interactions can also exist between the aliphatic portion of a flavor molecule and the siloxane surface of the silica.<sup>13,34,35</sup>

Adsorbed water will affect volatile retention. Water molecules will compete with other polar molecules for the SiOH sites on the silica surface.<sup>13</sup> Flavor retention may be improved



by pre-drying the silica before applying the flavor; however, the influence of moisture content on the retention of volatiles was not investigated in this study.

The efficiency of the silica to retain the model flavor decreased with higher flavor loads (Figures 6 and 7). At 50-66.7% flavor loads, the bulk of the flavor does not contact the silica surface (Table VI). Loss of compounds unable to associate with the silica surface is controlled by the pore size. The rate of flavor loss is less with the smaller diameter pore silicas (Syloid 74 and 244) because diffusion out of the silica pore is more restricted.

In general, for the three silicas evaluated in this study, the low molecular weight flavor compounds were lost first from the silica surface. Acetaldehyde and thiophene were not detected after two days. For the homologous series of esters in the model flavor, (ethyl acetate, ethyl propionate and ethyl butyrate), flavor loss decreased as the molecular weight increased (Figure 8). Similar results were observed for 2-hexanone and 2-octanone.

The increase in flavor retention for a homologous series of flavor compounds can be explained by the increase in size, boiling point and (at lower flavor loads) the proportion of the molecule interacting with the silica surface.

Differences in the degree at which flavor compounds are lost are not explained by boiling point alone (Figure 9). The amount of flavor maintained on the silica surface is also dependent on the polarity of the molecule. The unpaired electrons in 2-methyl pyrazine (BP 135°C), interact strongly with the silica surface. This is demonstrated by complete retention (at 20% flavor loads for all three silicas) of this molecule during storage.

As the flavor load increased, the retention of 2-methyl pyrazine decreased (Figure 9). At 50% flavor loads, 12-13% of the 2-methyl pyrazine was lost during plating. An additional 20% loss resulted after 38 days for the Syloid 74 and 244 silicas compared to a 58.6% loss on the Sylox 15 silica. The Sylox 15 silica plated at 66.7% flavor load lost 95.3% of the adsorbed pyrazine after 38 days.

The better retention of 2-octanone over benzaldehyde and heptaldehyde can be explained both by differences in polarity and volatility (Figures 6 and 7). Being more polar, 2-octanone out competes less polar compounds (benzaldehyde and heptaldehyde) for the available binding sites and is retained more effectively. Heptaldehyde is most readily lost since it is both less polar (than benzaldehyde and 2-octanone) and more volatile.

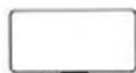
In contrast, limonene was not retained well on any of the silicas (Figure 10). The rate at which limonene was lost from the silicas (20% flavor) was comparable to M100 and Micropor Buds 1015A indicating minimal bond interaction between limonene and the silica surface.

Greater flavor retention on Syloid 74 and 244 silica versus Sylox 15 may also be attributed to higher chemical purity. The presence of small amounts of impurities are known to modify the surface of the silica.<sup>13</sup> Hydrated sodium ions located on the surface of the silica prevent hydrogen bonding. The concentration by weight of sodium

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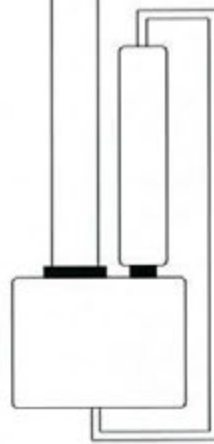
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(analyzed as sodium oxide) in Sylox 15 (6860 ppm) is approximately 10 times greater than that found in the Syloid 74 (640 ppm) or 244 (530 ppm) silicas (Table I). The higher level of sodium in the Sylox 15 may be another reason why less flavor is retained on this silica.

**Headspace Analysis**—The amount of a flavor compound present in the headspace of a sample at equilibrium would be dependent on the vapor pressure of the compound at the specified equilibrium conditions. An interaction between a flavor compound and a carrier would be reflected by a reduction in the vapor pressure of a flavor compound and a corresponding decrease in the headspace concentration.

No differences in the headspace concentrations were observed between the salt, sugars and carbohydrate carriers and equivalent amounts of model flavor (i.e. no carrier). However, flavor-carrier interactions were evident from the headspace analyses performed on the plated silica samples. An 80% reduction in equilibrium headspace concentration (at 35°C) was observed for the 20% Syloid 244 sample (with reference to M100 plated at a 20% flavor load, Figure 11). A lesser reduction (55%) in the headspace concentration was observed for the Sylox 15 silica loaded with 20% flavor (Figure 11). No differences in headspace concentration were observed between samples of the Syloid 74 and 244.

At higher flavor loads the magnitude of flavor-carrier interaction decreased as one might expect from the results of flavor retention study. For the Syloid 244 and 74 and Sylox 15 silicas loaded with 50% flavor loads the equilibrium headspace concentrations were reduced 60, 53 and 48%, respectively. The headspace concentration of the Sylox 15 sample loaded at 66.7% flavor was only 36.7% less than the equilibrium headspace concentration of an equal amount of model flavor.

These results demonstrate that headspace analysis of a plated silica sample can be used to evaluate a silica with respect to flavor-carrier interactions. A greater reduction in equilibrium concentration would predict better flavor retention-capabilities.

## Conclusions

The results of this study demonstrate that amorphous silicas evaluated in this study are more effective flavor carriers in the plating process compared to the traditional flavor carriers. While salt, sugar and carbohydrate carriers can carry from 3-20% flavor, the silicas evaluated in this study can carry from 1 to 2 times their weight in flavor and remain dry and free flowing.

The mechanism of flavor loss from salt, sugar and carbohydrate carriers occurred by simple evaporation, whereas the adsorption and retention of flavor compounds in amorphous silica was found to be more complex.

Some generalizations can be made for the three silicas evaluated in this study. Lower molecular weight flavor compounds are lost to a greater extent than higher molecular weight flavor compounds. Polar flavor compounds or compounds with unpaired electrons will strongly interact with the

silica surface and will be retained longer than nonpolar flavor compounds. Flavor retention in the silicas was dependent on flavor load. This suggests that a silica will have an optimum loading capacity with respect to flavor retention.

Oxidation of limonene occurred rapidly (4-10 days) on all of the salt, sugar and carbohydrate carriers. However, limonene had an extended shelf-life (24 to greater than 38 days) when adsorbed in the silica carriers. The ability of the silica to inhibit limonene oxidation was dependent on the type of silica. This implies that differences in physical and chemical properties of the silicas play an important role in the mechanism(s) responsible for protecting limonene against oxidation.

With respect to both flavor retention and oxidative stability of adsorbed flavor compounds, there is evidence that high chemical purity, small pore volume, small pore diameter and a large hydroxylated surface area are all desirable properties to consider when selecting amorphous silica as a flavor carrier.

Although amorphous silica has been used as a flavor carrier for over 20 years, very few studies have been published on the behavior of flavors plated on this type of carrier.

It is recognized that the scope of this study is limited to a select group of silicas and perhaps more optimum silicas are commercially available for application as flavor carriers. More studies are in progress to better predict the type and degree of flavor interactions with silicas of different particle sizes and surface chemistries.

The use of amorphous silica as a flavor carrier should be considered over the traditional flavor carriers in appropriate food-flavor applications.

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