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TBHQ, BHA/BHT 및 Methyl silicone이 식용유의 저장성과 고온에서의 안정성에 미치는 영향

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Effect of Methyl Silicone, TBHQ and BHA/BHT on Frying and Storage Stabilities of the Vegetable Salad Oil in High Density Polyethylene Bottles

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Summary

Functional additives such as methyl silicone, TBHQ and BHA/BHT have been evaluated for their effects on storage and frying stabilities of the vegetable salad oil.

All test results strongly suggest that methyl silicone improved the frying stability and TBHQ improved the storage stability. BHA/BHT improved neither storage stability, nor frying stability of the vegetable saladoil.

Based on the test results, it is recommended that methyl silicone in the range of 1.0±0.5ppm and TBHQ in the range of 200ppm be added to the vegetable salad oil for the improvement of frying and storage stabilities.

Introduction

Vegetable oil is highly susceptible to oxidation which affects the oil quality. Consequently, extreme care must be taken to avoid exposure of the oil to air from the start of oil processing to its consumption by consumers.

Currently, the oil is bottled in glass bottles and high density polyethylene(HDPE) bottles and is sold through distribution channel to consumers. Past experience has shown that the storage stability of the oil bottled in glass bottle was excellant, whereas the storage stability of the oil bottled in HDPE bottle wasy poor. The reason for the poor storage stability of the oil in HDPE bottle is due to the oxygen permeability of the HDPE bottle.

Most of the household oil consumption are for frying foods, and a batch of oil would be used repeatedly for economic reasons, when the oil is used as frying media. This will degrade the oil tremendously, since the oil is highly susceptible to oxidation at a frying temperature. It was also observed that the oil tends to develop undersirable foam due to oxidative polymerization when the oil is heated at a frying temperature. Objectives of this study are as follows;

(1) To evaluate the effects of various functional additives such as TBHQ, BHA/BHT, and methyl silicone on the storage stability of the oil in HDPE bottle stored at various temperatures (23, 32 and 38°C) for 12 months.

(2) To evaluate the effect of the additives on the frying stability of the freshly deodorized oil.

Experimental

1. Materials

The base oil in this study consisted of 95% partially saturated soy bean oil and 5% cotton oil and the additives were TBHQ and BHA/BHT(food grade) obtained from Eastman Kodak[1] and methyl silicone (Dimethyl polysiloxane) (food grade) obtained from Dow Corning[2]

2. Procedures

(a) Frying stability

To simulate the most extreme conditions that might be experienced by the consumer, the oil was heated to 195°C and 220 grams of french fries were fried intermittently after 15min, 5 hours of heat stress at 195°C in 1100 grams of the oil in the calibrated skillets. Then the oil was cooled to a room temperature and put in a 21 flask sealed with aluminum foil and placed in the dark cabinet overnight. Next morning, the oil was again heated to 195°C for 5 hours and the french fries (220 grams) were fried at the end of 5 hours of heat stress; first frying after 15 minutes of heat stress at 195°C, second frying after 5 hours of heat stress and third frying after 10 cumulative hours of heat stress.

The french fries and the oils were evaluated after each frying. The french fries were evaluated by expert panel for overall quality, color, greasy appearance, oil flavor, crispness and greasy mouthfeel. The oils were evaluated for foam formation during frying and for odor at the frying temperature during heat stress period. The oils after each frying were evaluated for chemical changes; Color (3a), free fatty acids (3b), iodine value (3c), AOM (3d), peroxide value (3e), trans isomers (3f), anisidine value (4a), fatty acid composition (4b), kinematic viscosity (4c) and polymers (5) were determined for chemical changes of the oils.

(b) Storage stability

The oil samples with various combination of the additives bottled in 1 gallon HDPE bottle were placed on storage test. The samples were stored for 12 months at 23, 32 and 38°C (73, 90 & 100°F) and were evaluated for their storage stability in terms of flavor, color and peroxide value.

Results and Discussion

A. Frying stability

1. Determination of optimal concentration of methyl silicone.

A series of pan frying test was conducted to determine an optimal concentration of methyl silicone. The concentration of methyl silicone tested were 0, 0.25, 0.5, 1, 2ppm. The base oil consisted of 95% partially saturated soy bean oil and 5% cotton oil.

(a) Evaluation of french fries

The results show that therer were no significant differences in overall quality, color, greasy appearance, oil flavor, crispness and greasy mouthfeel of the fries fried in the oils with different methyl silicone concentrations at each of three different heat stress times.

(b) Evaluation of oils

The oils(with different Me Si concentrations) were evaluated for foam formation during frying and for chemical changes (due to the oxidation and polymerization) such as color, FFA, totox (defined as 2× peroxide value+anisidine value), kinematic viscosity, iodine value and polymers after frying at the three different heat stress times.

While the control(without Me Si) showed a gradual increase in foam height to approximately 1/2" after 10 cumulative hours of heat stress, the Me Si added oils (0.25~2ppm) did not show any foam at all, even after ten cumulative hours of heat stress.

Fig. 1 shows the effect of Me Si concentrations on oxidation and polymerization of the oil at three different heat stress times. The degree of oxidation and polymerization appeary to be interrelated and was expressed in terms of color development, FFA, totox, polymers, iodine value and kinematic viscosity.

The results in Fig. 1 indicate that control was most severely oxidized and polymerized, and as Me Si concentration increased, the rate of oxidation and polymerization decreased asymptotically, indicating oxidative stability improved. Further, they appear to have improved to a greater extent in the range below 1ppm than in the range above 1ppm. Based on this result, it was decided to add 1 ppm methyl silicone to the oil in the subsequent frying and storage stability tests.

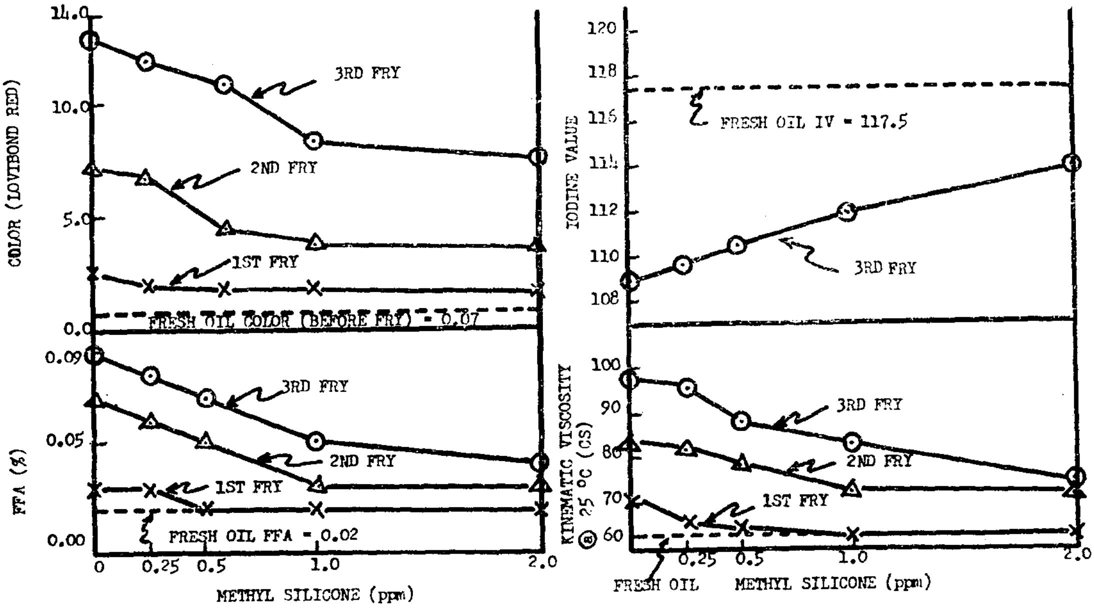

Fig. 1. Effect of methyl silicone concentration on frying stability of oil heat stressed at various time interval

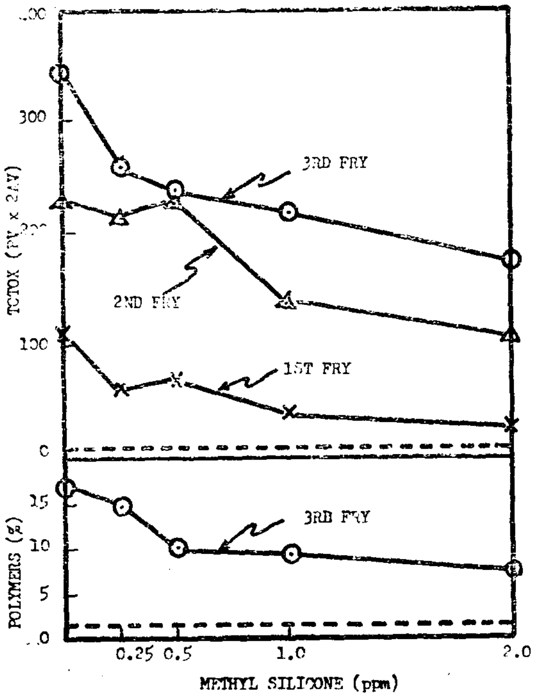

Fig. 1. Continued

Legend : ——— Before Fry (Fresh Oil)

×—× 1st Fry (15 Minutes After Oil Was Heated to a 195°C)

△—△ 2nd Fry (After 5 Hours of Heat Stress a 195°C)

⊙—⊙ 3rd Fry (After 10 Cumulative Hours of Heat Stress 195°C)

2. Effect of TBHQ, BHA/BHT, Methyl Silicone on Frying Stability

A series of frying test was conducted with samples shown in Table 1 to study the effect of the additives, independently & in combination, on the frying stability of the oil.

(a) Evaluation of French Fries

The french fries fried in the oils at 3 different heat stress times were evaluated by expert panel. Each of the response variables (overall quality, color, greasy appearance, oil flavor, crispness and greasy mouthfeel) was statistically evaluated. The results of the statistical analysis show that increasing heat stress time resulted in decreased overall quality and oil flavor rating.

(b) Evaluation of oils

The oils were evaluated for foam formation and odor at the frying temperature during frying. During the test, odor at the frying temperature was frequently monitored, and no off-odor due to the functional additives was detected for all additive added oils. Me Si-added oils (regardless of the presence of other functional additives such as TBHQ and BHA/BHT) did not show any foam at all when fries were fried in the oil heat stressed for ten cumulative hours at 195°C. On the other hand, the oils without MeSi

Table 1. Functional additive system for frying and storage stability studies.

Additives	Sample No.							
	1	2	3	4	5	6	7	8
Methyl Silicone (ppm)	0	0	0	0	1	1	1	1
BHA/BHT (ppm)	0	100/100	0	0	0	100/100	0	0
TBHQ (ppm)	0	0	200	100	0	0	200	100

began to show slight foam when the fries were fried in the oil heat stressed for five hours. When the fries were fried in the oils without MeSi heat stressed for ten cumulative hours, the foam was heavy (3/8″-1/2″ in foam height).

It was reported by Ota et al.[6], and confirmed by the above mentioned observation and anlytical results discussed below, that the foam formation of heat stressed oil without MeSi is caused by an oxidatively polymerized fraction, and MeSi added oil did not show any foam since MeSi reduced significantly the oxidative polymerization due to heat stress (i.e. 9.2% vs. 17.5% polymers for the oils without MeSi after ten hours of heat stress). Results on totox, AOM, IV, and kinematic viscoity shown in Table 2 strongly suggest that MeSi indeed reduces oxidation and polymerization of oil under heat stress at the frying temperature (195°C). Further, combination of MeSi and TBHQ appears to be synergistic in reducing oxidation and polymerization. Results on color shown in Table 2 indicate that MeSi retards oil color development over 10 cummulative hours of heat stress at 195°C and combination of MeSi and TBHQ again appears to be synergistic in this regard.

Free fatty acid content of MeSi added oil (regardless of the presence of TBHQ and BHA/BHT) increased

Table 2. Effect of TBHQ & Methyl Silicone on the frying stability of 95% soy/5% cotton blend oil at various stages of heat stress

Oil Sample	Totox of Oils Heat Stressed 195°C for:				AOM of Oils Heat Stressed 195°C for:			
	Before Fry	Initial	5 Hours	10 Hours	Before Fry	Initial	5 Hours	10 Hours
Control (No Additive)	2.3	66.6	246.2	262.2	20	10	4	4
200 ppm TBHQ	2.3	42.9	219.3	252.3	67	17	4	4
1 ppm MeSi	3.2	32.8	103.6	152.6	23	13	10	10
1 ppm MeSi+200 ppm TBHQ	2.5	19.5	69.9	106.1	50	51	14	12

Oil Sample	IV of Oils Heat Stressed 195°C for:				Kinematic Viscosity of Oils Heat Stressed 195°C for:			
	Before Fry	Initial	5 hours	10 Hours	Before Fry	Initial	5 Hours	10 Hours
Control (No Additive)	115.0	115.0	108.6	106.1	62	66	94	110
200 ppm TBHQ	115.4	115.8	109.4	107.2	62	64	89	104
1 ppm MeSi	115.6	115.4	113.8	111.9	63	66	72	80
1 ppm MeSi+200 ppm TBHQ	115.7	115.8	114.6	113.5	63	63	67	72

Oil Sample	Color of Oils Heat Stressed 195°C for:				P/S Ratio (Estimated) of Oils Heat Stressed 195°C for:			
	Before Fry	Initial (1st Fry)	5 Hours (2nd Fry)	10 Hours (3rd Fry)	Before Fry	Initial	5 Hours	10 Hours
Cotrol (No Additive)	0.8	2.3	4.5	11.0	2.3	2.3	1.9	1.8
200 ppmTBHQ	0.8	1.7	3.9	9.0	2.3	2.3	2.0	1.9
1 ppm MeSi	0.7	1.7	3.1	7.5	2.3	2.3	2.2	2.1
1 ppm MeSi+200 ppm TBHQ	0.8	1.8	2.4	4.4	2.3	2.3	2.3	2.2

only slightly from 0.03% to 0.05% over the ten cumulative hours of heat stress. In contrast, free fatty acid content of the oils without Me Si increased from 0.03% to a range of 0.07-0.1% after 5 hours of heat stress. After 10 cumulative hours, it ranged from 0.09%-0.12%. The increase in free fatty acid content appears to be mainly due to thermal degradation of triglyceride. The effect of hydrolysis on the free fatty acid increase must have been very slight, since only three batches of french fries were fried over 10 hours of heat stress.

Results on trans isomers indicate that presence of the functional additives did not affect the level of trans isomer formation due to the heat stress. It ranged from 19.2% to 20.6% and the average was 19.9%.

Fatty acid compositions (shown in Fig. 2 & 3) obtained from the unnormalized GLC for the oils with various combination of TBHQ, and MeSi at various stages of heat stress indicate that palmitic (C16 : 0), oleic (C18 : 1), linoleic (C18 : 2) and linolenic (C18 : 3) are the main fatty acids which varied in proportion to heat stress time; palmitic, stearic and oleic acids increased in proportion to heat stress period while linoleic and linolenic acids decreased. However,

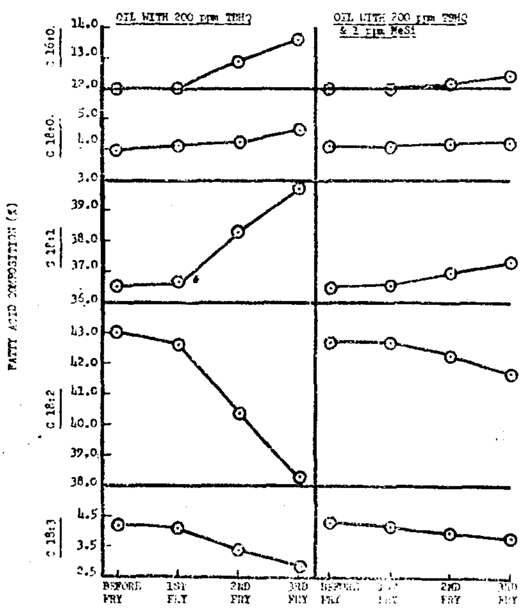

Fig. 3. Fatty acid composition of oil with 200 ppm TBHQ & oil with 200ppm TBHQ & 1 ppm Mesi

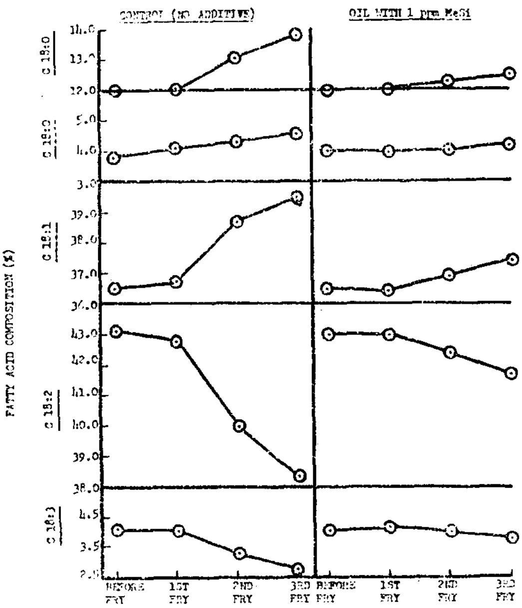

Fig. 2. Fatty acid composition of control & oil with 1 ppm Mesi

the changes for MeSi added oil were much less than those for the oil without MeSi. Based on the fatty acid composition and average trans isomers (19.9%), P/S(polyunsaturated fatty acids/saturated fatty acids) ratio for the additive oils at various stages of heat stress were estimated as shown in Table 2. Here again, the advantage of MeSi is apparent.

In summary, MeSi definitely improves the frying stability of the oil. Main function of the MeSi for the frying stability improvement appears to be to reduce the oxidation and polymerization at the frying temperature, thus resulting in less development of foam and color and resulting in less change in free fatty acid and P/S ratio.

Me Si also improved the flaver of the french fries. BHA/BHT or TBHQ, per se, did not affect the stability. But the combination of MeSi and TBHQ (200 ppm) rendered the best protection against oxidation and polymerization even though MeSi played the major role.

B. Storage stability

The oil samples with different combination of the functional additives as shown in Table 1 were put into 1 gallon HDPE bottles and were placed on a series of storage test at 23, 32 and 38°C (73, 90 &

100°F) for 12 months and were evaluated at two month interval for 12 months for flavor, PV and color. The samples were flavor tested by 10 expert panel using 9 point hedonic scale (9 is the blandest and 0 is the strongest flavor), color was measured by a Lovi Bond colorimeter.

1. **Flavor**

The results statistically analyzed by factorial design method has shown that Me Si and BHA/BHT did not affect the flavor of the oil. However, TBHQ (100 & 200ppm) affected the flavor of the oil as shown in Fig. 4. The results in Fig. 4. show that flavor of all samples decreased as the storage period was extended. Statistical analysis indicates that there was no significant difference in flavor score between control sample and TBHQ added sample up to the storage period of 4months. But from six months, flavor score of TBHQ added samples (100 & 200ppm) were decreased at a slower rate than the flavor score of control samples. The results in Figure 4 were differentiated into 3 different temperature levels to check the effect of TBHQ on the flavor of the oil at various temperatures during the storage periods. The results in Fig. 5 shows that the flavor of the oil was not affected by TBHQ for the oil stored at 73°F. However, the flavor of the oils stored at 90 and 100°F was affected by TBHQ after 6 months of storage period.

Fig. 6 shows the effect of storage temperature on flavor of oil (regardless of presence of TBHQ, BHA/BHT and Me Si). The results indicate that the storage temperature affected significantly the flavor of the oils. The high storage temperature caused the flavor degradation at much faster rate than the lower storage temperature.

2. **Peroxide Value** (PV)

Here again, methyl silicone and BHA/BHT did not

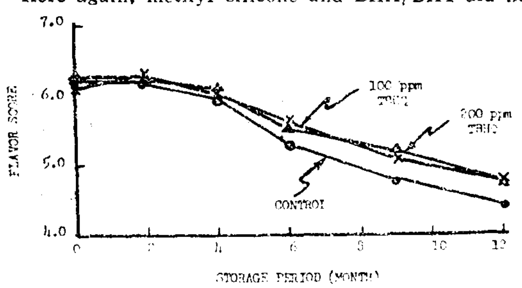

Fig. 4. Effect of TBHQ on flavor of oil at various storage periods

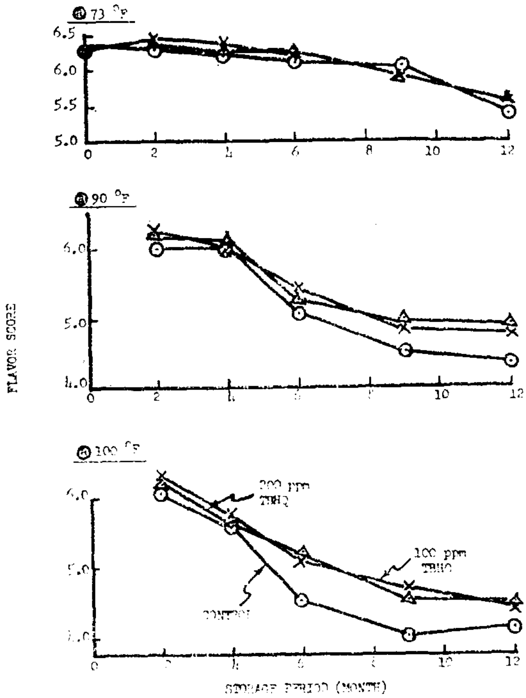

Fig. 5. Effect of TBHQ on flavor of oil at various storage tempertures & storage periods.

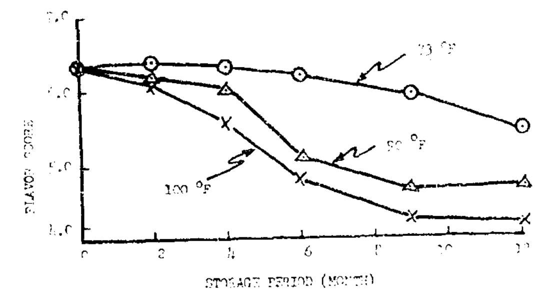

Fig. 6. Effect of storage temperature on flavor of oil at various storage periods

affect the PV of the oil. However, TBHQ at both levels affected the PV. Fig. 7 indicates that PV's of both control and TBHQ added sample increased as the storage period was extended. However, PV's of control sample increased at much faster rate than those of TBHQ added samples. Fig. 8 shows that the effect of storage temperature on PV of oil (regardless of the presence of TBHO, BHA/BHT and Me Si). The results show that the higher storage temperature caused higher PV, indicating primary oxidation occurred at much faster rate at the higher storage temperature.

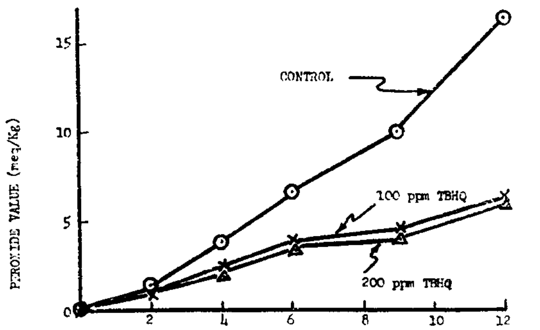

Fig. 7. Effect of TBHQ on PV of oil at Various Storage Periods

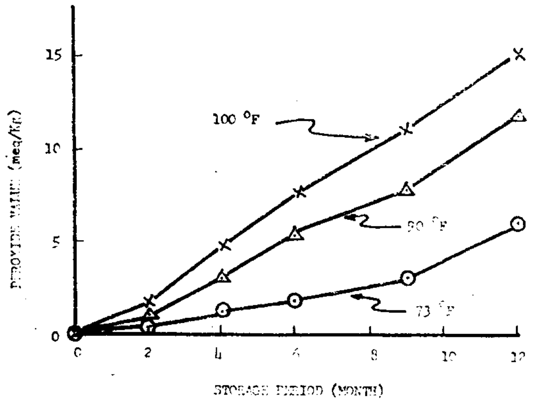

Fig. 8. Effect of Storage Temperature on PV at Various Storage Periods

3) Color

Color of the Oil samples was not affected by any of the additives evaluated in this study. However, the temperature level(23vs. 32vs, 38°C) and storage period (up to 12 months) affected the color of the oil (regardless of the presence of the additives).

Color of the oils stored at 23°C increased gradually to 1.5 red after nine month storage period and remained there after 12 months storage period. Color of the oils stored at 32°C increased to 1.5 red after four months storage period & remained there throughout the storage period. Color of the oils stored at 38°C increased abruptly to 1.5 red after 2 months storage period and remain there throughout the storage period.

In summary, Me Si and BHA/BHT did not improve the storage stability of the vegetable salad oil at all, when bottled in 1 gallon HDPE bottle. However, TBHQ improved the storage stability (in terms of falvor and PV) of the oil, when the oil is stored at higher temperatures. It cannot be emphasized too much that the role of TBHQ is only to retard the oxidation of the oil, resulting in extending the storage stability of the oil. Hence, the initial oil (before adding TBHQ) should be of good quality in order to maximize the effectiveness of TBHQ as an antioxidant.

Conclusion

Methyl silicone definitely improved the frying stability of the vegetable salad oil by reducing oxidation and polymerization at the frying temperature. This resulted in less development of foam and color and less change in free fatty acid and P/S ratio. Methyl silicone also improved the flavor of french fries. Further, combination of TBHQ and methyl silicone rendered the best protection against oxidation and polmerization, even though methyl silicone playedy the major role in reducing oxidation and polymerization. BHA/BHT or TBHQ, per se did not affect the frying stability.

Methyl silicone and BHA/BHT did not improve the storage stability of the vegetable salad oil at all, when bottled in HDPE bottle. However, TBHQ improved the storge stability of the oil, when the oil is stored at higher temperatures.

It is recommended that TBHQ (200ppm) and methyl silicone (1±0.5ppm) be added to the vegetable salad oil for its storage and frying stabilities, respectively.

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요 약

抗酸化劑인 TBHQ와 BHA/BHT와 消泡劑인 methyl silicone등이 식용유의 저장성과 고온에서의 안정성에 미치는 영향을 알아보기 위하여 一連의 실험을 하였다 실험결과 methyl silicone은 소포제로써뿐만 아니라 고온(195°C)에서의 산패를 방지하였고 저장성에는 별 영향이 없었으며 TBHQ는 식용유를 고밀도 polyethylene 병(용량 3.8l)에 넣어서 32°C와 38°C에서 1년간 저장했을 때 산패를 지연시켰으나 고온에서의 안정성에는 별 영향을 주지 않음을 알았다. 한편, BHA/BHT(100 ppm/100ppm)는 식용유의 저장성과 고온에서의 안정성

에 별 도움이 되지 아니하였다. 또한 methyl silicone 1±0.5ppm이 적정량(미국 FDA의 최대허용량 : 10ppm)이었으며 TBHQ는 FDA의 최대 허용량인 200ppm일때 가장 효과적임을 알았다.

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