Use of Silicones in Frying Oils[1]

I.P. FREEMAN, F.B. PADLEY and **W.L. SHEPPARD,** Unilever Research Laboratory, The Frythe, Welwyn, Herts, England

ABSTRACT

Silicones (polydimethyl siloxanes) greatly increase the oxidative stability of an edible oil at high temperature. The effect is demonstrated here, using a thin layer chromatography technique to follow the oxidation of the oil. The minimum fully effective concentration corresponds to a monolayer of silicone on the air-to-oil surface. Using an atomic absorption technique, estimates have been made of the amount of silicone picked up on food fried in a silicone-containing oil. When potato chips are fried in an oil containing 2 ppm silicone or more, the silicone content of the used oil is reduced to below 1 ppm and the surplus is taken up by the potato chips. In view of this pickup effect, and because only a very small amount of silicone is required to protect the oil, it is not desirable to use the silicone at levels higher than 2 ppm. Silicones should therefore be added in a controlled manner by the frying oil manufacturer.

INTRODUCTION

The use of silicone (polydimethylsiloxane) to suppress foaming in aqueous systems is well known and widely applied. Its use as an additive to frying oils is also becoming widespread although in this case the foam suppression is an indirect result of the inhibition of oxidation, which means that the buildup of foam-promoting oxidation products in the oil is suppressed.

The effect was first reported by Martin (1) who showed that a concentration of 0.03 ppm was sufficient to inhibit the oxidation of the frying oil as indicated by changes in a variety of physical and chemical properties of the oil over a prolonged heating period. Later, Babayan (2) showed that low concentrations of silicone would also raise the smoke point of an oil by as much as 25 F.

We have been studying the amounts of silicone necessary to give the protective effect using a thin layer chromatography (TLC) technique to follow the oxidation of the oil. The results confirm, in a sense, the efficacy of the low concentrations which Martin reported, but show that the surface concentration, rather than bulk concentration, is the quantity which governs the protective effect. The significance of this on the mechanism of protection is discussed.

Since the function of frying oils is to fry food, it is important to know the fate of the silicone in relation to the fried product. We have therefore investigated the extent to which silicone is picked up on food fried in a silicone-containing oil.

EXPERIMENTAL PROCEDURES

Materials

The oil used throughout the experiments was fully refined sunflowerseed oil. The silicone used was Antifoam A (Midland Silicones Ltd., U.K.). This material is typical of the silicone preparations supplied by various manufacturers for use in food products. Dispersions of silicone in the oil were prepared by adding the appropriate quantities of a 0.03% solution of silicone in hexane.

Analytical Methods

Thin layer chromatographic method for determining oxidized fat content: Thin layer plates were prepared in the usual way from Silica Gel G to give a layer 0.25 mm thick. The oxidized fat samples were applied to the plates in 10% chloroform solution, using 1 μl capillary applicators ("Microcaps"). The plates were developed with 1% ether in benzene to separate the unoxidized triglyceride from the oxidized and partial glycerides which run together. The spots were made visible by spraying with chromic acid and charring in an oven at 120 C for 20 min and were subsequently quantified by photodensitometry using a Joyce-Loebl "Chromoscan." The spots were standardized by comparison with fractions obtained from an oxidized oil using the column chromatography method of Quinlin and Weiser (3). The results have been expressed as per cent unoxidized triglyceride. No distinction has been made between oxidized fat, partial glyceride and nonsaponifiable.

Method of Estimating Silicone

Silicone concentrations were determined by atomic absorption spectroscopy. The instrument used was a Perkin Elmer Model 303 in conjunction with a high intensity (P.E. Intensitronic) Silicon Hollow Cathode lamp, a nitrous oxide-acetylene burner head, a Servomex mains voltage stabilizer and a 2.5 mV strip chart recorder. Also incorporated was a system to heat the "auxiliary air" supply. This was done by passing the gas through a spiral metal tube, around which was wrapped an electric heating tape. It was found that this led to increased sensitivity, probably due to better atomization.

The instrument settings used were as follows: wavelength, 2516° A; slit, 0.3 mm; acetylene pressure, 12 psi, acetylene flow setting, 6; nitrous oxide pressure, 30 psi, nitrous oxide flow setting, 13.5; scale expansion, x 30 (ultimate expansion x 120); noise suppression, 4.

The height of the burner was adjusted so that the center of the hollow cathode lamp light beam passed 0.8 cm above

TABLE I

Per Cent of Unoxidized Triglyceride

Day		Control	BHT	Silicone
1st	A.M.	85	85	85
	P.M.	75	74	86
2nd	A.M.	75	73	82
	P.M.	65	65	81
3rd	A.M.	59	60	80
	P.M.	62	65	79
4th	A.M.	63	62	79
	P.M.	58	56	75

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TABLE II

Per Cent Unoxidized Triglyceride (Experiment 1: 50 ml Beakers, Diameter, 3.6 cm)

Heating times, days	Silicone, ppm												
	1	0.1		0.06		0.05	0.04		0.03	0.02		0.01	0
		a	b	a	b		a	b		a	b		
0	89	87	88	88	91	83	89	89	87	88	89	87	85
1	84	86	87	88	88	—	86	90	85	86	90	83	72
2	84	82	81	81	84	85	80	82	84	—	82	80	68
3	—	80	—	81	81	—	82	82	80	80	—	64	59
4	76	—	—	—	78	75	76	78	74	76	79	62	57
5	—	75	73	73	80	—	—	75	—	—	76	—	56

[a]Without packing tubes.

[b]With packing tubes.

the surface of the burner.

The oil to be tested was sprayed as a 50% v/v solution in *n*-hexane. No advantage was found in warming the solution prior to spraying. Using the above conditions, a detection limit of 0.3 ppm silicone could be achieved, provided that an identical oil, free of silicone, was available as a control. In practice it was found that oils of different physical properties or oils which had been subjected to, say, different frying conditions had different spraying characteristics which made the background noise level very unpredictable. This reduced the working limit to 1 ppm for a semiquantitative result. An attempt was made to improve on this, using the low temperature extraction technique of Neal et al. (4). However it was found that the extracts obtained gave large and unreproducible variations in absorption, and this nullified the advantages of the concentration achieved.

Oxidation Experiments

Oxidations were carried out by heating the oil in open beakers at 180 C on a hot plate. Samples were taken out at intervals and the amount of oxidized material present was estimated by TLC.

In the first series of experiments, three samples of oil were tested: (a) a control oil with no additive; (b) an oil containing a conventional antioxidant, butylated hydroxy toluene (BHT) 0.02%; and (c) an oil containing silicone, 1 ppm.

Forty grams of each oil were put into three identical beakers and heated on a hot plate. The hot plate was kept at 180 C during the day (ca. 7.5 hr) and switched off overnight (ca. 15.5 hr) with ca. 30 min heating up and cooling down periods. This alternate heating and cooling effect would be expected to give more rapid deterioration of the oil than would an equivalent continuous heating period (5) and is similar to conditions prevailing in normal frying practice. The conventional antioxidant, by protecting the oil during the cool periods, might be expected to show to more advantage with the alternating regime than with continuous heating. Samples were taken from the oils in the morning and in the evening. These were analyzed for residual unoxidized triglycerides. The percentages of unoxidized triglycerides are listed in Table I.

The main oxidized component of a fat has an Rf value on TLC similar to diglyceride, and no attempt was made to separate them. To be absolutely correct, on the basis of our analytical method, oxidized oils include partial glycerides, oxidized triglyceride and nonsaponifiable material. At the start of an experiment, therefore, an oil does not have a value of 100% unoxidized triglyceride as a consequence of its partial glyceride content, etc.

There is a slight anomaly on the third day when the amount of unoxidized triglyceride appears to have increased during the heating period, but the general conclusion is clear. The conventional antioxidant has had no protective effect on the oil while the silicone has had a very marked protective effect. The inactivity of the antioxidant suggests that it has been substantially destroyed during the first hot period.

In the second series, equal quantities of oil, 30 g, were contained in identical beakers (50 ml beakers, 3.6 cm internal diameter), but different quantities of silicone, from 0 to 1 ppm, were added.

Some of the beakers were packed with small specimen tubes which were immersed in the oil, below the surface, to increase the oil to glass surface area without altering the oil to air surface area. The beakers were heated on a hot plate at 100 C. Heating was applied for 8 hr during the day and switched off overnight over several days. At the end of each day's heating period samples were taken and analyzed for percentage of unoxidized triglyceride using TLC.

In the third experiment, the same quantity of oil, 30 g, was contained in 250 ml beakers to give a larger oil to air surface area than in the 50 ml beakers. As before, various quantities of silicone were added to each beaker and heated on a hot plate at 180 C. As the oxidation rates in general were faster with the larger surface area, samples were taken every hour, during a single heating period.

The result of the 50 ml beaker experiments show (Table II) that for silicone contents of 1 ppm down to 0.02 ppm the oxidation rates are all very similar and significantly lower than when no silicone is present. At 0.01 ppm the rate of oxidation is at an intermediate level. This indicates that the silicones are giving their full protective effect at

TABLE III

Per Cent Unoxidized Triglyceride
(Experiment 2: 250 ml Beakers, Diameter, 6.5 cm)

Heating time, hr	Silicone, ppm				
	0.1	0.06	0.04	0.02	0
1	81	80	77	74	78
2	82	77	77	—	70
4	75	69	66	—	63
5	73	—	54	51	52
6	72	56	54	53	50
7	64	53	43	47	48
8	64	51	44	45	40

TABLE IV

Pickup of Silicone on Fried Food

Food	Silicone content of frying oil, ppm		Silicone content of food, ppm	
	Before frying	After frying	Extracted oil	Total food
300 g Chips in 1 liter SFO at 180 C for 10 min	1	0.5-1.0	0.5-1.0	0.005
	2	0.5-1.0	4-5	0.2
	5	0.5-1.0	40	2

0.02 ppm, but at 0.01 ppm there is insufficient silicone to give full protection.

The presence of the packing tubes has made no difference to the course of the oxidations, indicating that the area of the oil to glass surface has no significance.

In the 250 ml beaker experiment (Table III), 0.04 ppm silicone shows no protective effect and 0.06 ppm is not sufficient to give the full protective effect shown at 0.1 ppm. Thus in the 250 ml beaker the minimum effective concentration of silicone lies between 0.1 and 0.06 ppm, while in the 50 ml beaker the minimum effective concentration lies between 0.02 and 0.01 ppm. The 50 ml beakers (3.6 cm diameter) have oil to air surface areas of 10.2 cm^2, while the 250 ml beakers with diameters of 6.5 cm have oil to air surface areas of 33.2 cm^2. At these concentrations it is reasonable to assume that practically all the silicones will be in the surface. Thus the minimum effective surface concentration will lie between 0.06 and 0.03 $\mu g/cm^2$ in the 50 ml beakers and between 0.09 and 0.05 $\mu g/cm^2$ in the 250 ml beakers. In general, then, the minimum effective surface concentration must be between 0.06 and 0.05 $\mu g/cm^2$.

DISCUSSION

The results from the beaker experiments indicated that the effectiveness of the silicone was independent of the amount of silicone until this amount fell below 0.05-0.06 $\mu g/cm^2$ oil to air surface. Below this amount the effectiveness of the silicone dropped off rapidly. Assuming this critical amount of silicone represents a monolayer, the cross-section of the dimethyl siloxane monomer unit works out to be 20 to 25Å^2. This is in good agreement with the value of 20Å^2 obtained by Ellison and Zisman (6) using force-area measurements.

It can be concluded then that the protective effect is due to a monolayer of silicone on the oil to air surface. There are a number of possibilities for the precise mode of action of this monolayer. The simplest is that it forms a physical barrier preventing the penetration of oxygen into the oil. But this assumes that oxygen diffuses through the silicone layer less rapidly than through the surface layer of oil molecules, and there is no reason why this should be so. It is more likely that the oxidation normally takes place at the air-oil interface, and that the silicone presents a relatively inert surface to the atmosphere. It may even be that the silicone acts, in a sense, as a true antioxidant in that it oxidizes by an ionic mechanism and so inhibits the propagation of free radical chains. If this is the case, its effectiveness, compared with conventional antioxidants, will arise from its concentration in the surface where the oxidation occurs.

An alternative possibility rests on the fact that the silicone monolayer inhibits convection currents in the surface. This effect has been demonstrated by Bell in the case of paints, where silicones are used to inhibit pigment flotation (7).

The effect can be demonstrated in a beaker of hot oil by lightly sprinkling lycopodium dust onto the surface. Without silicone the convection currents rapidly sweep the dust from the surface. With silicone present, the dust remains undisturbed. The importance of convection currents in the oxidation of heated oil has been demonstrated by Rock and Roth (8), who showed that the rate of oxidation of the oil was dependent on the rate and duration of the convection currents. The result described above is in agreement with another result reported by Rock et al. (9), who found that silicone had a protective effect when the oil was heated from below by a hot plate, but not when heated in an oven. They attributed this effect to the difference in the temperature of the air-oil interface (100 C hotter in the oven), but it is reasonable to think that convection currents would be playing a part here also.

Whatever the mechanism, the inhibition of oxidation by silicone is a very real effect which is being usefully exploited for protecting frying oils. But in some circumstances the effect may not be so useful. The widespread use of silicone products for lubricating laboratory glassware coupled with the small amounts required to give an inhibiting effect add up to a real possibility that experiments designed to measure oxidation phenomena will yield anomalous results, unless the experimenters are aware of the effect and take precautions to avoid it.

Investigation of Fried Foods

Potato chips and fish fingers were fried in sunflower oil containing different levels of silicone. The adsorbed oil was extracted from the products in a soxhlet with ether and the silicone concentration estimated by atomic absorption as described above. The results for chips are presented in Table IV.

The concentration of silicone in the oil extracted from the fried chips increases as the concentration of silicone in the frying oil increases. The relationship is not linear, however, and the adsorption is probably not dependent on any partition effect, but more on a mechanical pickup of excess silicone from the oil. This occurs because of the low solubility (<1 ppm) of silicone. Droplets of excess silicone will therefore appear in the oil if the concentration is greater than ca. 1 ppm. This excess silicone will quickly adhere to any available surface, such as walls of the vessel or the surface of the fried product.

No detectable increased adsorption of silicone onto fish fingers was observed, and this is possibly due to the shorter frying time and the greater evolution of steam compared to chips. The adsorption of silicone onto chips, however, means that silicones should be added at a low level (1-2 ppm) in a controlled manner to frying oils.

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