Commercial spreads formulation, structure and properties

This article is by Gary List, K.R. Steidley, and W.E. Neff of the U.S. Department of Agriculture's National Center for Agricultural Utilization Research, 1815 N. University St., Peoria, Il 61604 (phone: 309-681-6388; fax: 309-681-6679). *The article is based on the presentation, "Formulation, Structure and Properties of Commercial Spreads, a 1999 Survey" by Mr. List during the 49th Oilseeds Conference held during March 2000 in New Orleans, Louisiana.*

11-01-2000
To: Susan Thompson
ONPLDS
FDA

Too long to fax - see chart last page - el fenid it hard to see a "lower trans" label

Daniel B. Cohen
2315 Shenandoah Place
Davis, California 95616

best -
Dan Cohen

During the past several decades, the margarine industry has undergone much change. Driven by consumer demands for fewer calories, standard 80% fat margarines have been replaced largely by so-called spreads containing 40–70% fat. Other factors affecting the industry stem from health and nutritional issues leading to the use of more liquid oils, thereby increasing levels of polyunsaturated fatty acids. The topic of *trans* acids resulting from hydrogenation will likely affect the industry as a result of labeling regulations recently proposed by the U.S. Food and Drug Administration. Historically, margarine, spread, and shortening oils have been formulated from a basestock system, employing a number of oils hydrogenated to standard iodine values (IV), melting points, and solid fat index (SFI) properties. The properties of these oils within a typical hydrogenated soybean oil basestock system are known, and blending these products, either with each other or in combination with liquid oil, permits the formulation of a wide variety of margarines/spread oils.

The primary quality control tools used by the industry employ SFI or solid fat content (SFC), determined by dilatometry and nuclear magnetic resonance, respectively. The structures of hydrogenated triglycerides have received little attention and, owing to the complexity of these products, fundamental questions including specificity for hydrogenation of the 1 or 2 position of triglycerides, as well as triglyceride selectivity, remain controversial topics.

Experimental

Margarines and spreads obtained from local supermarkets were transferred to glass beakers, placed in a microwave oven and, after melting, the oils were recovered by centrifugation. Fatty acid compositions were determined by capillary gas chromatography of the fatty acid methyl esters obtained by transesterification. Triglycerides were separated by high-pressure liquid chromatography (HPLC). Dropping points and solid fat index determinations were carried out according to official AOCS methods. Details of the procedure are available from the author.

The fatty acid composition and physical properties of seventeen commercial margarines and spreads are given in Table 1. Included are data for nine soft tub and eight stick products. SFI and drop melting points agree with previously published values. Excellent agreement was obtained between IV calculated from HPLC analysis of the triglycerides and those calculated from gas chromatography of the methyl esters. *Trans* acid content of the soft tub products ranged from 2.6–14.6% of the total fatty acid content, while the stick products ranged from 3.2–25.8%. A survey of the composition and properties of a number of soft tub margarines published in 1991 indicated that products formulated from hydrogenated soybean oil in the United States contained *trans* acids levels ranging from 10.3–12.4% of the total fatty acid con-

Table 1

Fatty acid composition and physical properties of 17 commercial margarines and spreads[a]

Sample	% fat	Oil components[a]	Solid fat index (°C)					Drop melting point (°C)	Iodine value		% *Trans* acids	Fatty acids by FAME–GC					
			10	21.1	26.7	33.3	40		TG–HPLC	FAME–GC		14:0	16:0	18:0	18:1	18:2	18:3
Tub																	
A	68	PHSO	10.4	5.8	4.0	2.1	0.3	32.7	101.2	104.3	14.6	0.0	10.8	6.1	47.0	34.5	1.6
B	80	L,PHSO	9.3	4.9	3.8	1.9	0.7	32.2	112.8	114.2	7.9	0.0	11.9	5.9	36.7	41.1	4.4
C	60	L,PHSO	8.3	5.4	4.3	2.5	1.4	31.2	118.3	119.1	5.3	0.1	11.5	7.3	30.8	44.3	6.1
D	70	L,PHSO	9.0	5.3	4.1	2.2	0.4	31.8	119.4	120.0	6.1	0.1	10.7	7.2	31.7	44.1	6.3
E	70	PHSO	11.5	6.6	3.7	1.7	0.1	32.6	98.0	99.9	14.5	0.1	12.6	6.5	47.3	32.0	1.5
F	48	L,PHSO	9.0	5.6	4.2	2.2	0.8	32.2	119.9	119.5	5.4	0.0	11.7	7.0	30.6	44.7	6.1
G	60	LSO,HSO PHSO,LCO	10.1	4.8	3.0	1.6	0.3	33.1	118.6	118.3	2.6	0.0	7.3	12.1	25.6	53.9	1.1
H	80	L,PHSO	13.9	8.6	4.7	0.7	0.6	31.5	110.7	115.3	10.5	0.0	10.5	6.4	38.0	39.5	5.6
I	60	L,PHSO	13.7	7.5	4.5	1.3	0.2	31.6	112.2	113.7	10.5	0.3	11.1	6.7	38.1	38.3	5.6
Stick																	
J	80	L,PHSO	24.8	13.0	7.7	1.7	0.1	33.0	79.5	82.9	25.8	0.2	13.5	6.1	64.8	15.1	0.4
K	70	L,PHSO	20.4	10.7	7.5	3.1	0.2	33.8	96.1	94.9	18.2	0.0	13.1	6.5	52.9	25.7	1.9
L	40	L,PHSO	19.7	10.3	5.1	0.3	0.2	31.8	94.7	96.7	19.0	0.0	12.3	5.7	53.9	26.4	1.8
M	68	LSO,HSO, PHSO,LCO	13.7	7.4	4.7	2.5	0.4	35.1	101.7	105.6	3.2	0.0	7.3	17.9	29.0	44.2	1.5
N	60	L,PHSO	19.3	9.0	5.6	1.7	0.1	32.1	96.8	97.8	16.7	0.0	13.2	6.1	51.2	26.4	3.1
O	70	L,PHCO	20.3	12.3	8.4	3.2	0.3	34.0	103.3	104.6	14.8	0.0	12.0	5.9	43.8	37.8	0.6
P	53	L,PHSO	21.6	12.0	7.9	2.5	0.3	32.9	91.8	95.7	18.2	0.0	11.5	8.1	51.9	26.7	1.9
Q	40	L,PHSO	22.4	12.4	8.8	3.0	0.2	33.7	90.4	95.0	19.7	0.0	10.8	7.8	54.9	24.6	2.0

[a] PHSO, partially hydrogenated soybean oil; L,PHSO, liquid and partially hydrogenated soybean oil; LSO, liquid sunflower oil, HSO, hydrogenated soybean oil; LCO, liquid canola oil, L,PHCO, liquid and partially hydrogenated corn oil; TG–HPLC, triglycerides by high-performance liquid chromatography; FAME–GC, fatty acid methyl esters by gas chromatography.

Table 2
Triglycerides of common vegetable oils by high-pressure liquid chromatography–flame ionization detection

Triglyceride[a]	Canola	Peanut	Corn	Cottonseed	Soybean	Mid-oleic sunflower	Regular sunflower
LnLnLn	0.1	0.0	0.0	0.0	0.0	0.0	0.0
LnLnL	0.3	0.0	0.0	0.1	0.7	0.0	0.0
LnLL	1.2	0.1	0.6	0.1	6.3	0.1	0.0
LnLnO	1.3	0.0	0.0	0.1	0.2	0.0	0.0
LnLnP	0.1	0.0	0.0	0.0	0.1	0.0	0.0
LLL	2.7	1.9	23.4	18.8	17.2	11.5	32.4
LnLO	6.4	0.2	0.9	1.2	5.0	1.0	1.1
LnLP	1.0	0.1	0.4	0.8	2.5	0.1	0.2
LLO	9.0	13.0	23.4	12.6	17.9	12.1	27.9
LnOO	9.6	0.4	0.5	0.5	1.3	0.9	0.4
LLP	3.0	3.8	15.7	27.8	12.9	4.1	10.7
LnOP	1.8	0.2	0.4	1.6	1.1	0.2	0.3
LnPP	0.1	0.6	0.3	0.3	0.1	0.0	0.2
LOO	21.7	20.1	10.9	3.7	9.5	8.3	6.7
LLS	1.0	0.9	2.1	1.8	3.2	2.7	7.4
LOP	5.8	11.8	10.4	12.9	9.2	2.6	4.8
PLP	1.1	2.8	1.7	10.8	1.6	0.1	0.7
OOO	23.6	15.7	3.3	1.0	3.1	40.2	1.7
LOS	1.3	2.4	1.5	0.8	2.7	1.6	2.2
POO	4.8	8.7	2.4	0.0	2.3	5.7	0.6
SLP	1.1	4.8	0.6	1.4	0.9	0.4	0.7
POP	0.3	1.8	0.6	1.3	0.6	0.8	0.8
PPP	0.3	1.0	0.2	1.9	0.1	0.1	0.1
SOO	1.4	3.0	0.4	0.1	0.7	5.4	0.4
SLS	0.3	1.6	0.2	0.2	0.2	0.3	0.3
SOP	0.4	1.4	0.2	0.2	0.3	0.3	0.3
PPS	0.1	2.0	0.1	0.1	0.1	0.1	0.1
SOS	0.1	0.7	0.1	0.0	0.0	0.9	0.1
PSS	0.0	0.7	0.0	0.0	0.0	0.1	0.1
SSS	0.0	0.2	0.0	0.0	0.0	0.2	0.0

[a]Ln, linolenic, L, linoleic, O, oleic, P, palmitic, S, stearic

tent; the *trans* content of Canadian margarines ranged from 12.6–14.1%

According to their labels, most of these products were formulated from either hydrogenated soybean oil or from blends of hydrogenated and liquid soybean oil. Although the fatty acid compositional data are in agreement with this approach, the individual triglyceride profiles provide additional information. The HPLC triglyceride profiles of a number of common unhydrogenated vegetable oils used in margarine/spread formulations are shown in Table 2.

Corn, cottonseed, soybean, and sunflower oil all contain three triglycerides that serve as markers to estimate the proportions of unhydrogenated oil used in margarine/spread oils. These include trilinolein (LLL), dilinoleyl-olein (LLO) and dilinoleyl-palmitin (LLP). Since HPLC will not resolve positional iso-

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mers, the LLO peak contains LOL as well. Because palmitic and stearic acid are essentially absent from the 2-position of vegetable oil triglycerides, the LLP peak contains very little LPL. Canola and mid-oleic sunflower triglycerides contain high levels of triolein and dioleyl-linolein which can be used as markers in margarine/spread oils. However, since triolein is a major product resulting from hydrogenation, its presence may complicate interpretation of the HPLC data, as will be discussed later.

The effects of hydrogenation on the triglyceride structure of vegetable oils have received little attention. At high pressures, where a hydrogen-rich environment exists on the catalyst surface, the linoleate-containing triglycerides LLL, LLO, and LLP are strongly adsorbed, favoring hydrogenation. At lower pressures other reactions take place, including isomerization from *cis* to *trans,* desorption from the catalyst surface and readsorption, where the cycle may be repeated. At high pressures (500 lb H_2) hydrogenation is truly nonselective, since di- and trisaturates are formed at IV of about 70. *Trans* acid levels are relatively low. At lower pressures (50 lb H_2) the reaction becomes more selective since di- and trisaturated triglycerides are essentially absent while the *trans* acid levels become elevated (22%).

Tub product G and stick product M (Table 1) are low-*trans* products containing 2.6 and 3.2% *trans,* respectively, and appear to be formulated by both interesterification and hydrogenation. The elevated stearic acid contents suggest that interesterified basestock(s) high in stearic acid were blended with liquid oils to achieve the desired solid fat index profiles. Of the nine tub products shown in Table 1, only two (A and E) are formulated from all-hydrogenated oils while seven are formulated from a single hydrogenated basestock and liquid oil. Oils high in LLL, LLO, and LLP are indicative of unhydrogenated oils in their formulations.

Stick products contain higher amounts of triolein (OOO) which are undoubtedly complex mixtures of both *cis* and *trans* isomers. Common liquid vegetable oils high in triolein include canola, peanut, and mid-oleic sunflower oil. However, soybean and corn oils are low in triolein, which increases upon hydrogenation. Thus high levels of triolein in a margarine/spread oil may result from either the liquid oil or the hydrogenated component.

Stick and spreadable stick products require higher SFI profiles than soft tub spreads, that limits the amount of liquid oil that can be incorporated into the formulation. For example, a typical tub margarine oil formulated from 25–30% hydrogenated soybean oil (IV 65) and 70–75% liquid oil will contain about 10% *trans* acids and have SFI values of 12 at 10°C, 4–5 at 21.1°C, and 2 at 33.3°C. To achieve SFI values suitable for stick and spreadable stick the ratio of basestock to liquid oil must be increased to about 50:50, thereby increasing the *trans* acids levels to about 20%. The data shown in Table 3 suggest that, while some liquid oils are incorporated into stick products, most are formulated from a multiple basestock system employing two or more hydrogenated oils.

Triglyceride data from the stick margarines/spreads are more difficult to interpret because hydrogenation decreases the amounts of LLL, LLO, and LLP which, in turn, are dependent on the conditions employed during hydrogenation. For example, the triglyceride profile of commercially prepared hydrogenated-winterized soybean oil (IV 107) showed LLL, LLO, and LLP contents of 4.2, 10, and 6.1%. With the exception of stick product N formulated largely by interesterification, all other products are consistent with formulation from largely hydrogenated oils as opposed to higher amounts of liquid oils used in tub products. Stick products are characterized by elevated levels of OOO, OOP, OOS and SSO, all of which are products resulting from the hydrogenation of LLL, LLO, and LLP.

The linolenic acid content of soybean oil is usually 7–8%. Thus, based on the data given in Table 1, soft tub products formulated with liquid and partially hydrogenated oils contain approximately 50–70% unhydrogenated oil, whereas the stick products contain about 20–30%. The trilinolein (LLL) content of unhydrogenated soybean oils we have examined varied from 15–19%. A heavily hydrogenated (IV 65–70) soybean oil basestock, suitable for blending with liquid soybean oil to formulate either soft tub or stick margarines, contains no trilinolein and, on this basis, the stick products shown in Table 1, with the exception of M and O, contain about the same amount of unhydrogenated oil as indicated from their linolenic acid contents. Samples K, L, P, and Q contain about 5% trilinolein (Table 3), which amounts to about 30% of the amount found in unhydrogenated soybean oil (Table 2).

The *trans* content of seven soft margarines/spreads taken over the years 1992–1999 are shown in Table 4. The data clearly show that industry has made a concerted effort to lower the *trans* acid levels of margarine/spread products. The average *trans* content in 1992 was 19.5% which dropped to 16.1% by 1995, and the present study

Triglycerides of margarine liquid oils by high-performance liquid chromatography

TAG[a]	Tub products									Stick products							
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
LnLnLn	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	01
LnLnL	0.0	0.4	0.8	0.7	0.0	0.8	0.2	0.6	0.7	0.0	2.0	0.2	0.2	0.3	0.1	0.0	0 0
LnLL	0.5	3.4	5.5	5.6	0.5	5.8	0.3	4.8	5.6	0.2	1.3	1.1	0 .2	2.7	0.5	1.1	1.4
LnLnO	0.5	1.0	0.2	0.7	0.4	0.5	0.0	0.7	0.1	0.1	0.3	0.4	0.1	0.3	0.1	0.5	0.3
LnLnP	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.2	0.2	0.0	0.1	0.0	0.2	0.1	0.1	0.0	0.0
LLL	3.6	12.6	14.3	14.5	3.8	14.8	26.3	12.1	12.4	1.0	5.1	4.8	17.9	7.5	13.5	5.1	4.8
LnLO	3.6	3.6	4.2	4.4	3.1	4.3	0.1	4.0	4.3	0.7	2.2	2.3	1.7	2.2	1.1	2.5	1.8
LnLP	0.7	1.7	2.3	2.5	0.6	2.5	0.4	2.2	2.2	0.2	0.8	0.8	0.4	1.2	0.3	0.9	0.8
LLO	9.3	13.4	14.3	13.9	10.3	13.6	21.0	12.0	12.1	2.4	7.1	6.7	15.9	7.5	14.0	7.5	6.3
LnOO	5.1	0.9	0.6	0.7	3.8	1.0	0.5	0.8	0.9	1.6	1.5	2.0	1.1	0.6	0.9	1.7	1.4
LLP	6.5	10.2	11.3	11.2	5.5	10.8	8.5	8.9	9.1	1.9	5.0	4.8	6.4	5.7	8.6	5.0	4.2
LnOP	2.1	0.6	0.7	0.5	1.3	1.0	0.6	0.9	0.8	0.5	0.8	0.9	0.7	0.5	0.9	0.9	0.6
LnPP	0.1	0.1	0.0	0.2	0.0	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.0
LOO	12.2	6.9	6.5	5.8	11.5	6. 1	5.3	5.4	5.4	7.4	5.8	5.8	5.0	4.4	7 0	6.0	4.8
LLS	6.1	3.0	3.2	3.2	6.9	3.1	5.9	2.6	2.7	2.5	3.7	3.8	4.9	2.8	1.6	3.7	4.8
LOP	13.6	8.3	8.0	7.6	11.5	7.5	5.0	6.6	6.7	10.8	7.3	8.1	5.1	5.9	7.2	7.5	6.9
PLP	1.6	1.7	1.7	1.7	1.5	1.7	0.7	1.5	1.5	0.1	1.1	1.3	0.8	1.5	1.3	1.4	1.1
OOO	5.4	4.3	2.8	3.2	5.5	4.0	2.4	3.6	2.6	23.3	21.2	30.7	2.9	23.3	9.9	18.0	23.4
LOS	8.5	7.1	5.9	5.7	7.7	5.6	4.8	8.0	9.7	4.7	14.1	3.9	5.9	8.3	12.8	15.2	12.5
POO	7.7	8.2	4.2	4.4	11.1	4.5	1.8	7.3	5.2	26.9	7.0	8.0	2.2	10.4	4.4	3.1	7.6
SLP	4.9	4.6	3.1	3.7	4.5	3.1	2.4	6.1	7.7	2.5	3.1	4.6	3.7	2.3	4.1	3.7	2.6
POP	1.6	2.2	1.3	1.3	1.8	0.8	1.2	1.0	1.4	1.4	1.4	0.0	1.1	2.0	0.7	2.1	0.9
PPP	0.1	0.0	0.2	0.3	0.8	0.2	0.1	0.9	0.4	0.0	2.5	3.4	0.2	0.6	0.0	0.8	0.8
SOO	2.2	3.0	3.3	1.9	2.1	2.0	2.8	1.7	1.7	6.5	4.7	3.6	5.0	5.2	1.8	4.4	6.1
SLS	1.8	0.5	1.4	3.1	2.7	2.7	2.3	4.3	3.8	1.0	1.5	1.3	4.1	1.7	5.6	4.4	2.1
SOP	1.6	1.5	2.1	2.1	2.4	1.9	2.3	2.2	2.0	3.5	1.1	0.9	3.8	2.2	2.0	3.5	3.5
PPS	0.0	0.1	0.2	0.1	0.2	1.0	4.3	0.2	0.5	0.1	0.2	0.4	9.3	0.2	0.9	0.8	0.2
SOS	0.4	0.2	1.2	0.7	0.5	0.1	0.3	0.8	0.1	0.2	0.4	0.1	0.8	0.3	0.1	0.1	0.7
PSS	0.1	0.1	0.2	0.1	0.1	0.0	0.0	0.2	0.0	0.2	0.3	0.0	0.2	0.2	0.0	0.0	0.2
SSS	0.1	0.3	0.2	0.0	0.1	0.1	0.1	0.0	0.0	0.2	0.3	0.1	0.3	0.1	0.1	0.1	0.1

[a] TAG, triglycerides; Ln, linolenic; L, linoleic; O, oleic; P, palmitic; S, stearic

Table 4
***Trans* content of soft margarines/spreads by year**

	Year			Overall
Brand	1992	1995	1999	reduction (%)
1	19.4	15.9	14.5	25.3
2	10.3	18.2	7.9	23.4
3	12.2	7.8	2.6	79.7
4	31.4	16.2	14.6	53.6
5	11.6	19.5	6.1	47.5
6	24.6	14.7	10.5	57.4
7	29.5	20.2	5.3	82.1
Average	19.9	16.1	8.8	55.8

shows an average of 8.8%, amounting to a 55.8% total reduction in *trans* acids over the seven-year period.

A survey of the composition and physical properties of North American stick margarines, published in 1989, showed that canola-based margarine produced in Canada contained 33.1–45% *trans*, whereas soybean oil-based margarine contained 22.4–30.1% *trans* (average 26.8%). Data for U.S. stick products (Table 1) show an average of 16.9% *trans* which includes the 3.2% sample. The other seven samples average 18.8% *trans*. Thus, over the past decade, the *trans* content of U.S. stick margarines has been reduced by 37%.

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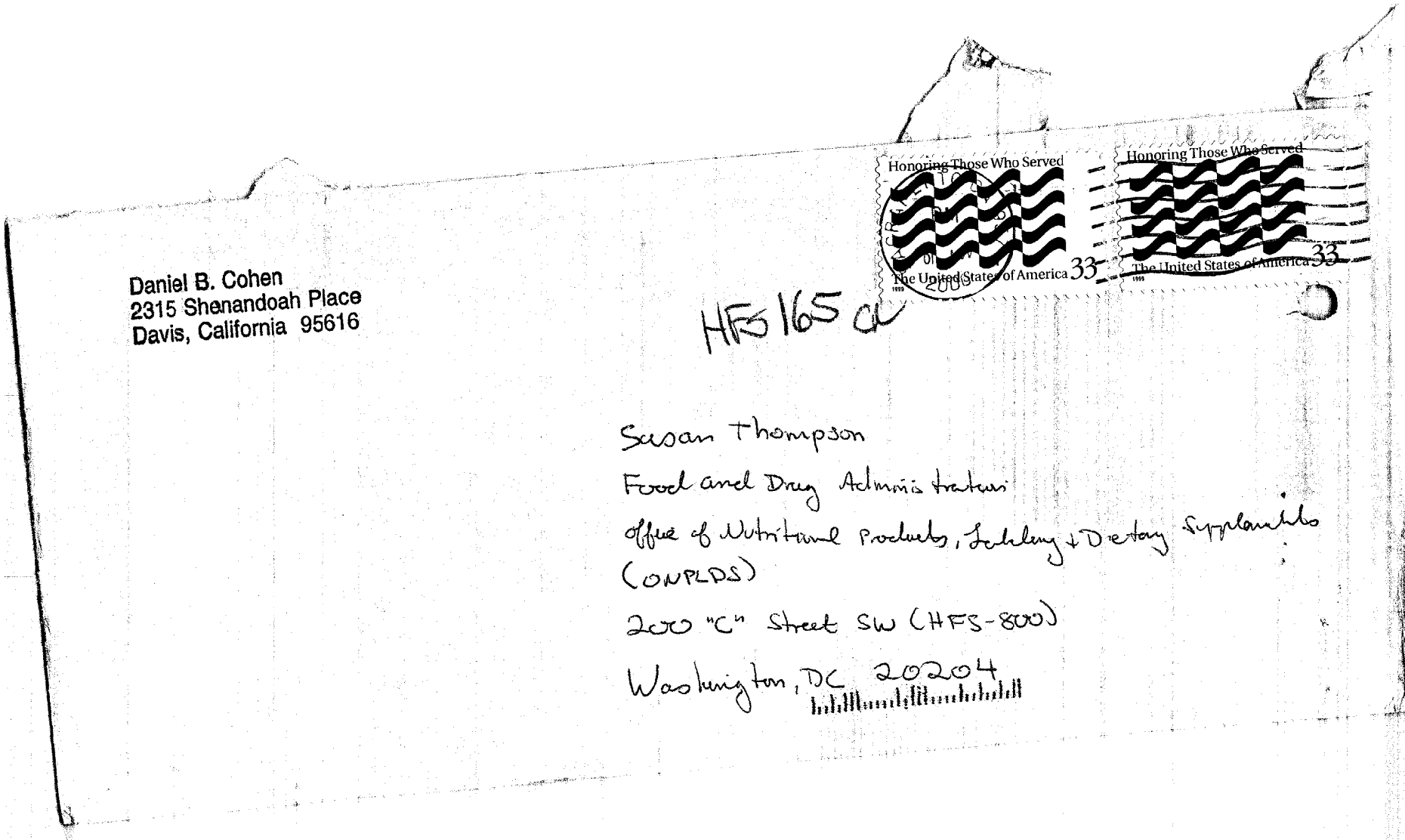
Daniel B. Cohen
2315 Shenandoah Place
Davis, California 95616
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Susan Thompson
Food and Drug Administration
Office of Nutritional Products, Labeling & Dietary Supplements
(ONPLDS)
200 "C" Street SW (HFS-800)
Washington, DC 20204