

# Flavor Reversion in Soybean Oil

## II. The Effect of Atmospheres of Different Oxygen Concentrations on the Flavor Reversion of Soybean Oil<sup>1,2</sup>

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EFFORTS to locate the source of the objectionable flavors and odors which appear in soybean oil under many conditions are hampered by the lack of any objective methods for following flavor deterioration. In a previous study (1) on the spectral changes occurring during the light-accelerated reversion of soybean oil, it was noted that an absorption band appeared at 234  $m\mu$ , the intensity of which increased as reversion and autoxidation progressed. This study has been continued in order to determine whether the selective absorption at 234  $m\mu$  could be correlated with the reversion process. To obviate the possibility that the spectral changes were the result of autoxidative reactions alone it was necessary to attempt the production of reverted flavors in inert atmospheres. The development of off-flavors and odors in fats and oils under conditions where oxidation would be reduced to a minimum has been reported on several occasions. Robinson and Black (2) found that hydrogenated soybean oil would undergo reversion in an atmosphere nearly free of oxygen. Bailey (3) observed that objectionable flavors appeared in hydrogenated lard after very slight oxidation. Bickford (4) reported that light-exposed soybean oil deteriorated in flavor when maintained under the vacuum of a mercury vapor diffusion pump. The flavor change that resulted in this way was described as different from that occurring in air. This observation has been extended in the present investigation to include an examination of the flavors produced by the light reversion of soybean oil under atmospheres of different oxygen concentrations.

### Experimental

The soybean oil used in this investigation was a commercial alkali-refined grade.<sup>3</sup> It was deodorized by the method of Bailey and Feuge (5).

Peroxide values were determined by a modified Wheeler method (6) and are expressed as milliequivalents of sodium thiosulfate per kilogram of fat. The Beckman quartz spectrophotometer was employed to measure the absorption spectra of isooctane solutions of the soybean oil.

The organoleptic observations were made by a panel of six well-trained individuals as previously described (1).

**Light Exposure.** Ten ml. samples of the soybean oil were poured into 100 ml. Petroff culture flasks (7) equipped with gas inlet and outlet tubes. Each flask and contents were inserted horizontally into a water bath maintained at 45.5°C. and submerged until

the top of the flask was about one-quarter inch below the surface of the water. A 250-watt G-E reflector-drying lamp (8) was placed three inches above the water level and centered directly over the Petroff flask. A slow stream of the desired gas, oxygen, tank nitrogen containing 0.5% oxygen or nitrogen purified by passage over heated copper turnings, was passed through the flask during the light exposure.

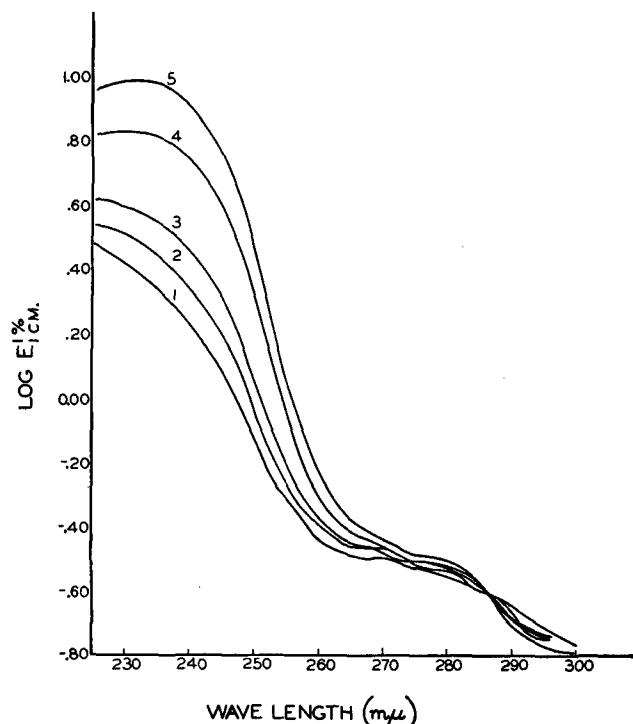


FIG. 1. Absorption curves of refined and deodorized soybean oil after exposure in air and in nitrogen to visible radiation.

1. Original oil.
2. Exposed sixteen hours under nitrogen.
3. Exposed forty-five hours under nitrogen.
4. Exposed eight hours in air.
5. Exposed sixteen hours in air.

### Results and Discussion

#### Changes in the Ultraviolet Absorption Spectrum of Soybean Oil Produced by Light Exposure

Curves 2 to 5 of Figure 1 show the spectral changes produced in soybean oil (Curve 1) when exposed in air and in nitrogen to the intense visible radiation of the G-E reflector-drying lamp. The appearance of a maximum at 234  $m\mu$  in the samples exposed in air (Curves 4 and 5) confirm previous observations (1). It will be noted that samples of the oil exposed to the visible radiation in an atmosphere of nitrogen do not develop the maximum at 234  $m\mu$  characteristic of the samples exposed in air. The simplest explanation of these observations is that the selective absorption at

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TABLE I  
The Oxidation of Soybean Oil Under  
Different Atmospheres

Time	Peroxide Value			
	100% O <sub>2</sub>	21% O <sub>2</sub>	0.5% O <sub>2</sub>	0% O <sub>2</sub>
hrs.				
0	0.7	0.7	0.7	0.7
0.5	6.8	4.7	2.1	....
1	14.8	9.1	2.1	....
2	28.2	16.3	2.8	....
4	63.6	33.3	4.0	0.8
8	132	76.6	6.4	1.7

234 m $\mu$  is due to oxidation products rather than the "reversion compounds" (1) of soybean oil.

#### Effect of Atmospheres of Different Oxygen Concentrations on the Flavor Changes Produced by Light Exposure

The data in Table I show the peroxide development in samples of soybean oil when exposed under varying oxygen concentration to the G-E reflector-drying lamp.

As expected, the oxidation rate decreased with decrease in oxygen concentration above the sample. Minute traces of oxygen were apparently present in the purified nitrogen as shown by the very slight but definite rise in peroxide value following very long exposures under the purified nitrogen.

Under each set of conditions it was found that reversion flavors were detectable after one-half hour of exposure. It may also be observed that under nitrogen, the reversion appeared at very low peroxide values. The various samples shown in Table I were examined organoleptically in three ways.

First, the effect of increasing exposure time on degree of reversion was noted. In each atmosphere studied, it was found that the reversion flavor became more pronounced as the exposure period increased.

Second, the samples exposed for equal lengths of time were compared with each other. Little or no

difference could be detected between samples of oil maintained in oxygen and in air for the same period of time, despite the difference in their peroxide values. However, a marked difference was noted between the above samples and those exposed under nitrogen. The former acquired the grassy flavor generally associated with reversion, but in the latter, grassy flavors, though evident, were accompanied and superseded by a particularly disagreeable and persistent drying aftertaste not readily detectable in the soybean oil reverted in air or oxygen. Oil exposed under nitrogen for very long periods developed a flavor that resembled heat-reverted oil.

Finally, pairs of oil samples with approximately equal peroxide values were compared with each other. In general, it was found that the samples exposed for the greater length of time were more strongly reverted.

#### Summary

It is evident that the oxidation rate of soybean oil may be varied over a considerable range without influencing the organoleptic evaluation of the degree of reversion. Even when the rate of oxidation is greatly reduced by the use of inert atmospheres, there is no diminution in the tendency to revert. On the contrary, with low oxygen concentrations, a type of reversion is produced that is more persistent in taste than that resulting in air or oxygen.

#### REFERENCES

1. Golumbic, C., Martin, C. J., and Daubert, B. F., *Oil and Soap*, **23**, 187 (1946).
2. Robinson, H. E., and Black, H. C., *Ind. Eng. Chem.*, **37**, 217 (1945).
3. Bailey, A. E., *Oil and Soap*, **33**, 55 (1946).
4. Bickford, W. G., *Oil and Soap*, **38**, 95 (1941).
5. Bailey, A. E., and Feuge, R. D., *Ind. Eng. Chem., Anal. Ed.*, **15**, 280 (1943).
6. Wheeler, D. H., *Oil and Soap* **9**, 89 (1932).
7. Petroff, S. A., *J. Lab. Clin. Med.*, **16**, 315 (1930).
8. Porter, L. C., *Agr. Eng.*, **25**, 148 (1944).

## Extraction and Purification of Gossypol from Cottonseed Meats\*

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THE literature indicates that some investigators (3) have encountered difficulties in precipitating gossypol extracted from cottonseed according to the modified method of Clark (5) and consequently have first extracted the oil from the crushed cottonseed with petroleum ether as described by Carruth (2, 3, 7). Murty, Murty, and Seshadri (7) developed another method, after finding their yields unsatisfactory with the latter, in which the gossypol was extracted from crushed cottonseed meats and precipitated with aniline. The dianilino-gossypol was converted to gossypol acetate by boiling for a few minutes with acetic anhydride. Boatner (2) reports that she was unable to remove all the red pigment from gossypol by two recrystallizations as the acetate and as gossypol, respectively.

Clark's methods of extraction (5) precipitation and purifications (6) have been satisfactory in this laboratory with certain modifications in technique to facilitate the procedure. A somewhat detailed description of the method is given because gossypol is precipitated with difficulty, if at all, unless precautions are taken to prevent its over-heating or scorching in the oil-ethyl ether extract; it is necessary to use peroxide-free ether at all times. (Ether in a wash bottle was repeatedly found to contain peroxides after standing in the laboratory a few days.)

#### Preparation of Cottonseed or Cottonseed Meats

Freshly crushed or rolled decorticated kernels or meats from prime quality seed collected before entering the cooker are screened as free from hulls as possible by means of a wire screen of 16 meshes per square centimeter and extracted with peroxide-free

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