

perature difference with difference in composition.

LITERATURE CITED

1. Armstrong, E. E., et al. J. Soc. Chem. Ind., 44: 1925, 63-68T.
2. Grün, Ad. and Janko, J. Deut. Oel u.

3. Fett-Ind., 41: 1921, 553-556, 572-574.
4. Francis, F., Piper, S. H., and Malkin, T. Proc. Roy. Soc. (London), 128A: 1930, 214-232.
5. Francis, F., and Piper, S. H. J. Am. Chem. Soc., 61: 1936, 577-581.
6. Francis, F., Piper, S. H., and Collins, J. J.

7. E. Proc. Roy. Soc. (London), 158A: 1937, 619-718.
8. Findlay, A., The Phase Rule and Its Applications. Longmans, Green and Co., London, 1931. 7 ed.
9. Shriner, R. L., Fulton, J. M., and Burks, D. Jr. J. Am. Chem. Soc., 55: 1933, 1494-1499.

Sodium Bisulphite As A Stabilizer For Hydrogenated Cottonseed Oil Shortening

By K. S. HOOVER and H. E. MOORE

CAPITAL CITY PRODUCTS CO., COLUMBUS, OHIO.

Abstract

Hydrogenated, deodorized cottonseed oil shortening, may be given increased keeping time and lowered peroxide values, if treated with small amounts of NaHSO_3 (either the dry powder or a saturated solution). The flavor of the treated shortening will be good if not too much bisulphite is used. The shortening so treated will contain a very small amount of SO_2 .

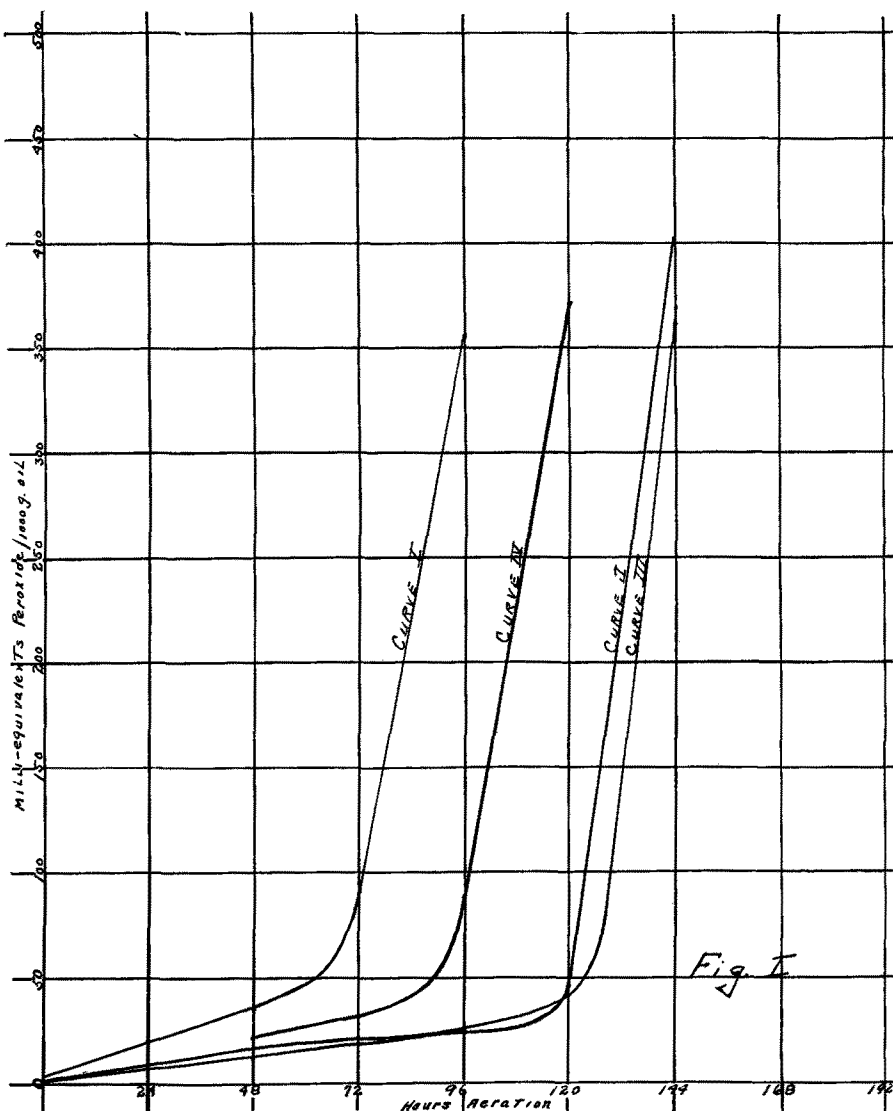
A LARGE number of aldehydes, ketones and organic peroxides are known to react with sodium bisulphite. Since these compounds are responsible, or at least partially so, for rancidity in edible oils and fats, the present investigation was undertaken to determine whether or not an oil or fat which had been treated with sodium bisulphite would have a lowered peroxide value, and to determine whether or not the keeping time of such a fat would be prolonged.

An extensive search of the chemical literature revealed very little information regarding the effects or results obtained when edible oils or fats are treated with sodium bisulphite.

This material has been used in the preparation of phenylhydrazine, (1), to prevent the formation of dark resinous or tarry residues. It has also been used to prevent the oxidation of alkaloids and of adrenalin in aqueous solution.

Moureau and Dufraisse have published a number of papers on Autoxidation and Anti-oxidases (2) (3) (4) (5) (6). Several of these papers concerned themselves with the catalytic properties of sulphur and its compounds. Although they have investigated the autoxidation and anti-oxidative properties of a large number of both organic and inorganic sulphur compounds, they do not give data regarding the action of sodium bisulphite on oils or fats.

Simmons and Mitchel (7) men-



tion the fact that sodium bisulphite, which possesses the property of combining with aldehydes, has been utilized in some cases for deodorizing oils and fats with good results.

Experimental

The fat used in these experiments was a fifty-pound can of hydrogenated deodorized cotton seed oil Shortening, which had the following chemical and physical

characteristics:

Iodine number	65.8
Melting Point (closed capillary)	108° F.
Congeeing Point	31.0° C.
Saponification number	197.8
Peroxide value (Millequivalents per Kilo)	1.8
Lovibond Color ..	20 yel.—1.45 red
Free Fatty Acid	0.03%
Flavor	good

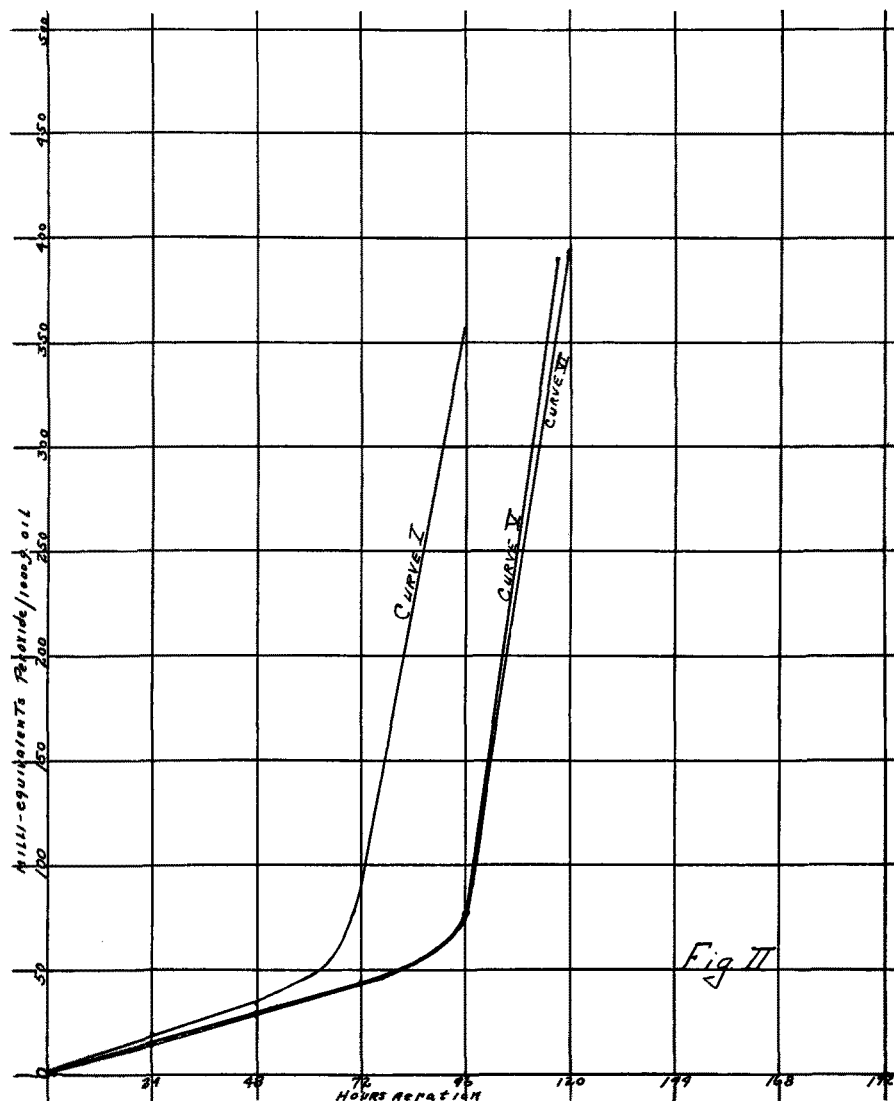


Fig II

The sodium bisulphite used was Baker — C.P., which upon analysis proved to be 95.6% NaHSO₃.

Saturated solutions of this material were prepared by dissolving approximately 65 gms. of NaHSO₃ in 100 c.c. distilled H₂O.

The shortening to be treated with sodium bisulphite (either the dry powder, or the saturated solution) was accurately weighed into a two liter pyrex glass beaker. It was then melted and heated to 120° F. Sodium bisulphite was added, and the mixture vigorously stirred with a glass agitator for the required time.

The mixture was then filtered several times through the same paper (E-D No. 617) to remove excess NaHSO₃.

Samples of the treated shortening were then taken and peroxide value determinations were made. Since the methods for these determinations are well known, and there are abundant references in

the literature, the method need not be given here.

Accelerated keeping tests were then made on the treated shortening, using the Swift Stability apparatus. (8)

The following experiments were carried out.

Experiment No. 1

Original Shortening

Six tubes of original shortening described above were placed in the stability apparatus. One tube was taken out every twenty-four hours and the peroxide value determined.

Peroxide value	Time in hours
1.8	0
20.0	24
34.0	48
88.0	72
356.0	96

A peroxide value of 120 was taken as the rancid point. The keeping time on this sample was seventy-four hours. (See curve I, Figure 1.)

Experiment No. 2

The same shortening was used as in Experiment No. 1.

1500 gms. of shortening were treated for fifteen minutes at 120° F. with 2 c.c. of a saturated aqueous solution of NaHSO₃. The resulting product was allowed to stand five minutes and then filtered twice through rapid filter paper (E-D No. 617). It came out bright and clear.

Color, after treatment
 20 yel. — 1.5 red
 Free Fatty Acid after treatment 0.04%
 Flavor .. Tasted strongly of SO₂.
 Peroxide value negative

Samples were placed in the stability apparatus as described above and the following results were obtained.

Peroxide value	Time in hours
.0	0
9.0	24
16.0	48
21.0	72
24.0	96
46.0	120
402.0	144

The keeping time is 125 hours. (See curve II, Figure 1)

The treatment increased the keeping time about fifty hours, but gave a bad flavor to the product.

Experiment No. 3

The same shortening was used as in Experiment No. 1. 1500 gms. of shortening were treated for fifteen minutes at 120° F. with 1 c.c. of a saturated aqueous solution of NaHSO₃ and allowed to stand five minutes and then filtered through rapid filter paper.

It came out bright and clear.
 Color after treatment
 20 yel. — 1.45 red
 Free Fatty Acid after treatment 0.04%
 Flavor after treatment
 tasted of SO₂ but not as strongly as experiment No. 2

Peroxide value none

Samples were placed in the stability apparatus and the following results obtained.

Peroxide value	Time in hours
0	0
6	24
12	48
18	72
26	96
41	120
362	144

The keeping time is about 138 hours. (See curve III, Figure 1.)

TABLE I

Amt. of NaHSO ₃ Used	Amt. of Shortening Used	Length of Time Agitated	Keeping Time	Increase in Keeping Time	Flavor of Treated Shortening	Peroxide Value of Treated Shortening	Amt. Peroxide Value Lowered	Keeping Test Curve
2 cc. Sat. Solu.	1500 gms.	15 min.	125 hrs.	50 hrs.	Like SO ₂	0	1.8	Curve II Fig. I
1 cc. Sat. Solu.	1500 gms.	15 min.	138 hrs.	64 hrs.	SO ₂ like	0	1.8	Curve III Fig. I
1 cc. Sat. Solu.	1500 gms.	1 hour	98.4 hrs.	24 hrs.	SO ₂ like	0	1.8	Curve IV Fig. I
15 gms. dry pwd.	1500 gms.	1 hour	100 hrs.	26 hrs.	Good. No. SO ₂	0.42 ME	1.38	Curve VI Fig. II
1.5 gms. dry pwd.	1500 gms.	1 hour	98 hrs.	24 hrs.	Good. Not like SO ₂	0.4 ME	1.4	Curve V Fig. II
½ cc. Sat. Solu.	1500 gms.	1 hour	122 hrs.	48 hrs.	Slightly of SO ₂	0.25 ME	1.55	Curve VII Fig. III
¼ cc. Sat. Solu.	1500 gms.	1 hour	122 hrs.	48 hrs.	Good. No. SO ₂	0.4 ME	1.4	Curve VIII Fig. III
1/10 cc. Sat. Solu.	1500 gms.	1 hour	105 hrs.	31 hrs.	Good. Not like SO ₂	1.0 ME	0.8	Curve IX Fig. III

The treatment gave an increased keeping time (about sixty-four hours) but flavor was not good enough.

A number of experiments were then carried out, using various amounts of NaHSO₃, (both the dry powdered material and the saturated solution). Table I will show the results obtained.

An inspection of the table reveals that ¼ cc. of a saturated solution of NaHSO₃ will increase the keeping time of 1500 gms. of shortening about forty-eight hours and will lower its initial peroxide value about 77%.

The saturated solution of sodium bisulphite used in these experiments had a specific gravity of about 1.34 and contained approximately 39% NaHSO₃.

Since the saturated solution of bisulphite had a specific gravity of 1.34, one fourth of a c.c. would then weigh 0.335 gms., which is 0.0223 of 1% of the weight of shortening used, or on the basis of 100,000 pounds of shortening, 22 pounds of a saturated solution of NaHSO₃ should be used. This 22 pounds of saturated solution would contain about 8½ pounds of dry NaHSO₃.

In conclusion, if a quantity of hydrogenated deodorized cottonseed oil shortening is treated with a small amount (about 0.022 of 1%) of a saturated solution of NaHSO₃, its peroxide value will be lowered, and its keeping time increased substantially. The flavor of the treated product will be good if not too much of the saturated solution of bisulphite has been used.

The shortening so treated will contain very small amounts or traces of sulphur dioxide.

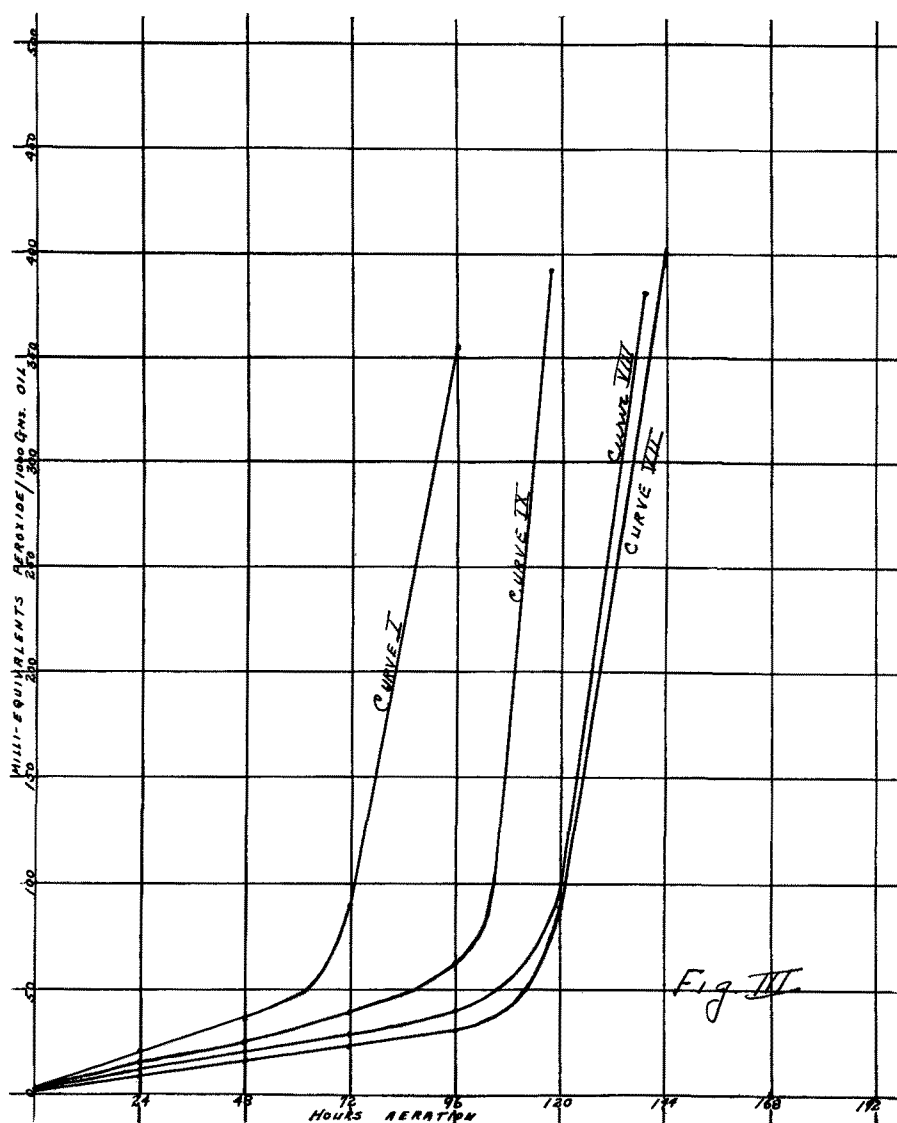


Fig. III.

- (1) R. H. Hamilton, Jr. — J. Am. Chem. Soc. 56, 487, 1934.
- (2) Moureau and Dufraise — Compt. Rend. Soc. Biol. 86, 321,03 (1922).
- (3) Moureau and Dufraise — Compt. Rend. — 174, 258-64 (1922).
- (4) Moureau and Dufraise — Rev. Sci. 60, 120-3. C. A. 16, 1439/9.
- (5) Moureau, Dufraise and Badoche — Compt. Rend. 179, 237-43 (1924).
- (6) Moureau and Dufraise — Compt. Rend. — 178, 1861-4 (1924).
- (7) Simmons and Mitchell — "Edible Fats and Oils." Page 47, Second Edition.
- (8) King, Roschen and Irwin — "Oil and Soap," — 10, 105-9 (1933).