

Obviously this method cannot replace the determination of total conjugated diene by infrared or ultraviolet spectroscopy, but it can supplement it, and it is the only method presently available to measure separately conjugated *cis-trans* and *trans-trans* compounds. When used in conjunction with a total diene determination, an estimate of conjugated *cis-cis* unsaturation may be obtained by difference.

The method has been used to follow the conversion of conjugated *cis-trans* octadecadienoate, obtained by alkali isomerization of linoleic acid, to the *trans-trans* isomer under the influence of several catalysts and under different conditions.

Summary

Pure conjugated methyl *cis-trans* and *trans-trans* octadecadienoates have been prepared and used to develop a method for the determination of these compounds by infrared spectrometry. *Cis-trans* compounds alone or in the presence of *trans-trans* conjugation may be determined directly by the absorption at 10.55 μ . In the absence of *cis-trans* isomers conjugated *trans-trans* octadecadienoates may be determined directly from the absorption at 10.11 μ . When both types of compounds are present however, a correction must be applied for the contribution of the *cis-trans*

isomers to the 10.11 μ absorption of the *trans-trans* material.

Acknowledgments

The authors are grateful to the Archer-Daniels-Midland Company for making available to them the infrared spectrophotometer used in these studies, and to George Mizuno for many of the spectral measurements.

REFERENCES

- Nichols, P. L. Jr., Herb, S. F., and Riemenschneider, R. W., *J. Am. Chem. Soc.*, **73**, 247 (1951).
- Ahlers, N. H. E., Brett, R. A., and McTaggart, N. A., *J. Appl. Chem.*, **3**, 433 (1953).
- Brice, B. A., and Swain, M. L., *J. Opt. Soc. Amer.*, **35**, 532 (1945).
- Gunstone, F. D., and Russell, W. C., *J. Chem. Soc.*, 1955, 3782.
- Hulst, van der, L. J. N., *Rec. trav. chim.*, **54**, 639, 644 (1935).
- Kass, J. P., in Mattiello, J. J., "Protective and Decorative Coatings," vol. IV, ch. 12, John Wiley and Sons Inc., New York, 1944.
- Witnauer, L. P., Nichols, P. L. Jr., and Senti, F. R., *J. Am. Oil Chemists' Soc.*, **26**, 653 (1949).
- Jackson, J. E., Paschke, R. F., Tolberg, W. E., Boyd, H. M., and Wheeler, D. H., *J. Am. Oil Chemists' Soc.*, **29**, 229 (1952).
- Allen, R. R., *J. Org. Chem.*, **26**, 143 (1956); *J. Am. Oil Chemists' Soc.*, **33**, 301 (1956).
- Tolberg, W. E., and Wheeler, D. H., *J. Am. Oil Chemists' Soc.*, **35**, 385 (1958).
- Privett, O. S., private communication.
- Smith, D. C., and Miller, E. C., *J. Opt. Soc. Amer.*, **34**, 130 (1944).
- Paschke, R. F., Tolberg, W. E., and Wheeler, D. H., *J. Am. Oil Chemists' Soc.*, **30**, 97 (1953).

[Received May 11, 1959]

The Design, Construction, and Operation of a Pilot-Plant-Size Plasticizer for Shortening and Margarine

B. S. HARRINGTON, R. W. BATES, and D. V. STINGLEY, Armour and Company, Chicago, Illinois

IN 1940 THE SENIOR AUTHOR of this paper designed and constructed a small plasticizer for plasticizing 12-ounce samples of shortening. This unit was in use in our pilot plant for a number of years in our experimental work. In 1957 it was decided that a larger unit would have greater utility, serving both for our experimental work and the preparation of actual samples for sales distribution. It was agreed that a three-pound size would have the greatest utility. Further, some refinements in design and construction seemed in order. Accordingly a unit was designed and built. Figure 1 shows a picture of the unit in its entirety except for the bath of cooling water. Figure 2 shows the cross-section of the chilling unit itself. Essentially it is a jacketed cylinder cooled with circulated ice water, in which a piston actuated by a steam pump moves at a rate of 12 strokes per minute. The product being plasticized is forced through a small adjustable slot in the piston as it moves from one end of the cylinder to the other. At the completion of the desired period of time, the slot is closed, a port is opened at the top end of the cylinder, and the product is forced into a receiving can.

To operate, the melted sample is placed in container A with the piston E at the top of the stroke. Valve C is closed. Valve B is opened, and shaft D is tightened down. The lever is engaged to the speed reducer, and the piston E is pulled down. The lever is disengaged temporarily as the sample is drawn into the chilling chamber F. Valve B is then closed, and shaft D is rotated one full turn. The lever actuating the steam

pump is engaged, and the piston goes up and down 12 times per minute, forcing the product through orifice G. At the completion of the cycle, shaft D is tightened when the plunger is at the bottom and the lever actuating the pump is disengaged on the up-stroke. Valve C is opened, and the product is forced into a convenient receiver. Air may be admitted near the end of the cycle by opening valve B momentarily as the piston E is on the downward stroke. Some of the dimensions of the various parts are given in Figure 2.

The cooling is effected by allowing brine to pass through a copper coil submerged in a water bath. The usual temperature of the water is 34–36°F. The water is circulated with a one-half-in. Viking pump. The motor used to run the pump is one-fourth horse power. The motor also actuates the cam (through a speed reducer), which engages the lever for actuating the steam pump. The steam pump used is a Burnham 6 $\frac{1}{8}$ x 12 in. Obviously other types would serve just as effectively. We have 125–140 p.s.i. steam pressure available in our pilot plant. The stroke is designed to bring the piston flush with the top and lower surfaces of the chamber. Retention of the product in the unit is less than 1%, which is easily removed by allowing the piston to move freely with the aperture closed by depressing shaft D and alternately opening and closing valves B and C. Where flavor is of prime importance, the unit may be flushed with salad oil or with some of the product to be plasticized.

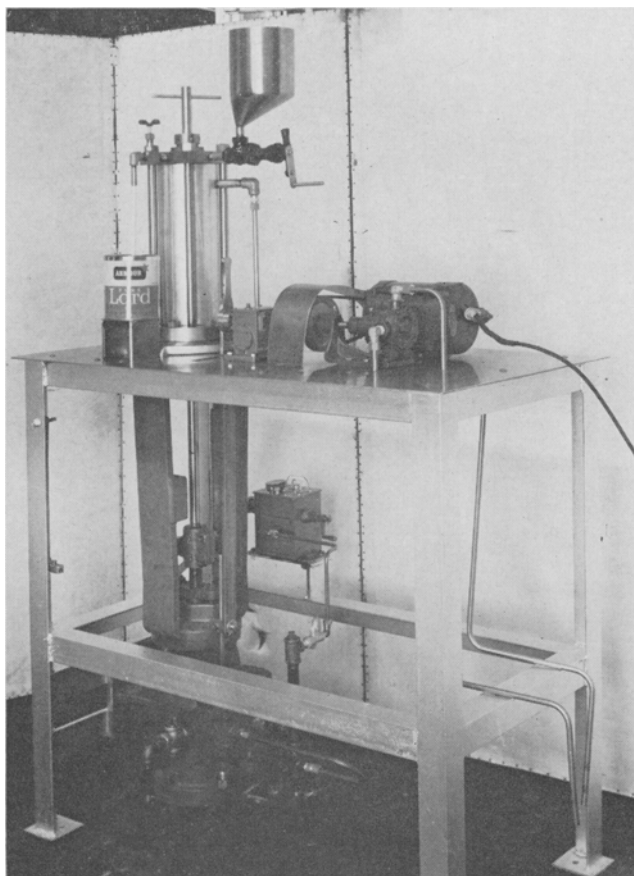


FIG. 1.

It was quite obvious that the plasticizing operation must be standardized. Several variables were immediately apparent which could or would affect the plasticity or appearance of the plasticized product, *viz.*: temperature of the input oil, temperature of the plasticizer jacket, time of plasticizing, size of sample, and control of air content of the plasticized sample. The items will be discussed in turn.

Obviously any reasonable temperature, at which the fat is liquid, may be chosen; 160° F. was chosen since at that temperature the fat does not accumulate on the sides of the container (A). To keep the temperature of the plasticizer jacket reasonably constant, the water bath is maintained at 34–36° F. by the circulating brine. Prior to using the unit, the brine-cooled water is circulated 20 min. The chamber of the plasticizer will hold a maximum of about 1,500 of fat. A 900-g. sample was used to demonstrate the effect of the time of plasticizing on the air content of the shortening. This amount of fat would permit quantities of air to enter the cylinder. Table I shows the air content of ordinary, dry-rendered lard, plasticized from one to 15 min. in the unit.

TABLE I
Time of Plasticizing vs. Air Content
Sample weight, 900 g.; sample, lard

Temperature as filled (°F.)	Time of plasticizing (min.)	% Air (by volume)
88.....	1	5
86.....	2	10
82.....	3	15
82.....	4	18
80.....	5	27
80.....	6	30
75.....	15	34

The air was admitted in all cases one minute before withdrawing the product. The air content varied from 5 to 34%. The effect of the size of the sample on the air content was studied. Table II shows the air content of plasticized lard, using from 700 to 1,500 g. and a plasticizing time of four minutes in all cases.

TABLE II
Sample Weight vs. Air Content
Plasticizing time, 4 minutes; sample, lard

Filling temperature (°F.)	Sample weight (g.)	% Air (by volume)
78.....	700	24
76.....	800	23
78.....	900	22
80.....	1000	19
80.....	1100	17
80.....	1200	15
80.....	1300	12
80.....	1400	6
80.....	1500	1

Using a four-minute plasticizing cycle, it is apparent that about 1,300 g. are optimum if the conventional air content of 12% is desired.

Keeping the sample weight at 1,300 g., tests were made on two more or less conventional types of bakers' shortening to show the plasticity of the products as measured by the penetration (A.S.T.M.) at 70° F. (1). The two products used were a conventional hydrogenated vegetable oil shortening and one made with a meat-base of modified lard and beef fats. The results are given in Tables III and IV.

TABLE III
Time of Plasticizing vs. Penetration at 70°F.
Sample weight, 1,300 g.
Product, hydrogenated vegetable oil with a solid fat index of
29.9 (50°F.), 21.2 (70°F.), 15.5 (92°F.), 9.2 (104°F.)
Tempering of filled products: 48 hrs. at 83°F., 40 hrs. at 70°F.

Time of plasticizing (min.)	A.S.T.M. penetration 70°F. (1) (mm./10)
1	78
2	104
3	142
4	148
5	153
6	168
10	174
Control—Plant plasticized (Votator) using 2B units (2)	146

On the basis of the results given in Tables III and IV, it is quite apparent that four minutes of plasticizing, using a 1,300-g. sample gave products comparable to those produced through a conventional plant Votator.

Using the operating conditions given in Table V, various samples of shortening were plasticized and tempered under the following operating conditions:

TABLE IV
Time of Plasticizing vs. Penetration at 70°F.
Sample weight, 1,300 g.
Product, meat-fat shortening with a solid fat index of 28.6 (50°F.)
21.9 (70°F.), 15.7 (92°F.), 10.6 (104°F.)
Tempering of product, 48 hrs. at 83°F.; 49 hrs. at 70°F.

Time of plasticizing (min.)	A.S.T.M. penetration 70°F. (mm./10)
1	84
2	100
3	156
4	165
5	168
6	170
10	176
Control—Plant plasticized (Votator), using 2B units	163

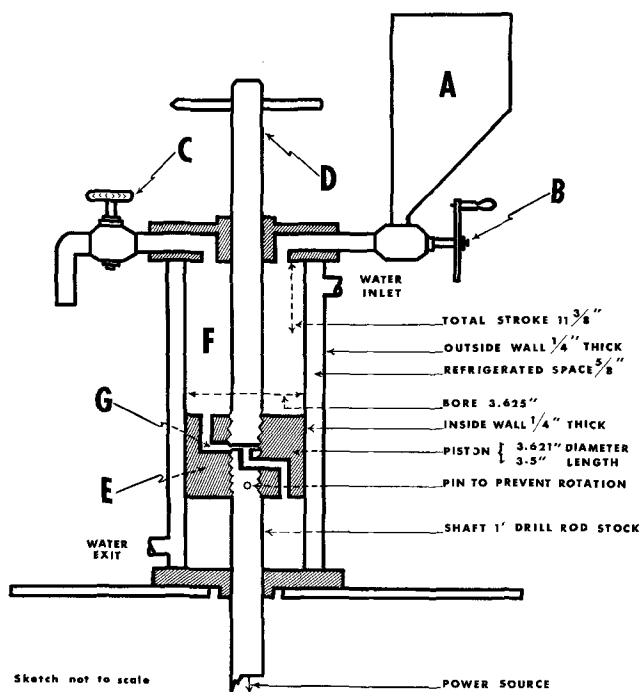


Fig. 2. Sectional view of pilot plant plasticizer—Armour and Company.

inlet oil temperature, 160° F.; cooling-water temperature, 34° F.; sample weight, 1,300 g.; time of plasticizing, 4 min.; and tempering, 48 hrs. at 83° F. Baking tests made on these samples are shown in Table V.

It is quite apparent that the performance of products plasticized through the pilot plant unit compares favorably with those obtained with plant-Votated products.

Some tests described in Table VI were made with our conventional high-ratio shortenings, comparing their performance with identical products plasticized through a plant Votator. Plasticizing conditions were

TABLE V
Performance and Plasticity Data

Sample	Air (% by vol.)	A.S.T.M. penetration 70°F.	Lb. cake volume pilot plant plasticized ^a	Lb. cake volume plant plasticized ^a
A.....	12.2	156	256	255
B.....	13.1	162	260	262
C.....	12.4	165	262	254
D.....	13.0	160	278	268
E.....	13.0	158	250	254
F.....	12.2	168	265	258

^a Armour method: Units reported are in ml./100 g. of cake.

the same as used on the shortening described in Table VI.

All results are given in ml. per 100 g. Both employ the Armour Method. It should be quite obvious that margarine can easily be prepared in the unit by adding all of the ingredients through container A. Should the unit be used extensively for margarine work, internal construction of stainless steel would be recommended.

TABLE VI
Performance—High Ratio Type Shortening

Sample	Pilot plant plasticized		Plant plasticized	
	Icing volume	Layer cake volume	Icing volume	Layer cake volume
1.....	126	286	126	287
2.....	120	290	124	296
3.....	128	291	126	292
4.....	135	288	139	293
5.....	130	288	133	286
6.....	133	274	131	278

Summarizing, a pilot-plant plasticizer has been designed and built which will plasticize a 1,300-g. sample in four minutes, giving a product very similar in performance and consistency to a plant-plasticized product. The unit is quite useful for the preparation of samples for sales service as well as for research purposes.

REFERENCES

1. Rich, A. D., *J. Am. Oil Chemists' Soc.*, 19, 54 (1942).
2. Slaughter, J. E., and McMichael, C. E., *J. Am. Oil Chemists' Soc.*, 26, 623 (1949).

[Received April 20, 1959]

The Preparation and Properties of Some Urethane Foams from Castor Oil and Elaidinized Castor Oil¹

D. A. YEADON, A. R. MARKEZICH, and L. A. GOLDBLATT,² Southern Regional Research Laboratory,³ New Orleans, Louisiana

THE PREPARATION and properties of a series of semi-rigid to soft urethane foams made from formulations containing 50, 60, 70, and 80% of castor oil have been previously reported (6). The present study is concerned with the effect of variation in the degree of crosslinking on properties of castor oil urethane foams and with a comparison of foams prepared

from elaidinized castor oil with analogous foams prepared from untreated castor oil.

Increasing the degree of crosslinking in urethane foams from castor oil should improve water resistance and shrinkage properties besides enhancing strength and hardness. The extent of crosslinking in castor oil urethane foams can be adjusted in the prepolymer preparation by varying the duration and temperature of reaction to permit formation of more allophanic ester groups. A series of foams was made and tested from prepolymers prepared this way from castor oil in which increased amounts of crosslinks were ap-

¹ Presented at the 50th Annual Meeting of the American Oil Chemists' Society, New Orleans, La., April 20-22, 1959.

² Present address: Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Albany, Calif.

³ One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.