TABLE VI

Composition of Methyl Esters Obtained from Phospholipids by Methanolysis and by Saponification-Fatty Acid Recovery

Phospholipids source	Method	Fatty acid composition						
		1=	2=	3=	4=	5=	6=	Sat.
		%	%	%	%	%	%	%
Plasma M, human	M[a]	37.8	11.6	3.1	4.5	1.1	2.0	39.9
	S[b]	40.6	11.0	3.2	4.4	0.9	1.7	39.1
Cells M, human	M	22.6	10.0	2.9	16.3	2.5	2.4	43.3
	S	23.7	9.5	2.8	14.9	2.6	2.8	43.7
Liver L. chick	M	11.0	21.1	2.5	21.5	2.4	2.4	39.1
	S	9.9	21.4	2.6	20.9	2.3	2.4	41.5
Liver, rabbit	M	19.6	29.0	2.1	7.5	1.2	0.8	40.0
	S	22.6	28.9	2.2	6.5	1.0	0.7	38.0
Soybean	M	14.4	42.8	8.5	0.0	0.0	0.0	34.3
	S	19.4	41.5	6.7	0.0	0.0	0.0	32.4

[a] Methanolysis, 10 ml. 0.1 N potassium methoxide, 1½ hrs. reflux, chromatographed.

[b] Saponification, extraction of unsaponifiables, and recovery of fatty acids.

fats and oils requiring only 5 min. of reflux time were described.

Quantitative conversion of fatty acids to methyl esters was accomplished by direct esterification with absolute methanol containing 4% HCL or H_2SO_4 and by methylation with diazomethane.

REFERENCES

1. Herb, S. F., Magidman, P., and Riemenschneider, R. W., J. Am. Oil Chemists' Soc., *37*, 127 (1960).
2. Kritchevsky, D., and Anderson, M. E., J. Am. Chem. Soc., *74*, 1857 (1952).
3. Luddy, F. E., Turner, A. Jr., and Scanlan, J. T., Anal. Chem., *25*, 1497 (1953); *ibid. 26*, 491 (1954).
4. "Organic Syntheses," Collective Vol. 2, pp. 165–167, John Wiley and Sons, New York, 1948.
5. Riemenschneider, R. W., Luddy, F. E., and Morris, S. G., J. Clin. Nutrition, *6*, 587 (1958).
6. Rollet, A. Z., Physiol. Chem., *61*, 210 (1909).
7. Shinowara, G. Y., and Brown, J. B., Oil and Soap, *15*, 151 (1938).
8. Stoffel, W., Chu, F., and Ahrens, E. H., Anal. Chem., *31*, 307 (1959).

[Received April 8, 1960]

Changes in Iodine Value and Refractive Index of Fatty Acids During Alkyd Resin Manufacture and Analysis

**P. J. SECREST and M. K. KAPRIELYAN, Analytical Research Department,
Sherwin-Williams Company, Chicago, Illinois**

IN MANY specifications for alkyd resins, limits are placed on the iodine value and refractive index of the separated fatty acids. Values obtained by various laboratories are not always in agreement. No work is known in which changes in iodine value and refractive index of fatty acids during alkyd resin manufacture and analysis have been studied and reported. This paper is a report of an investigation undertaken to determine the effects of alkyd resin manufacture and analysis upon the iodine value and the refractive index of fatty acids.

Experimental

Materials. One lot each of commercial linseed fatty acids, soya fatty acids, and low rosin (1%) tall oil fatty acids was selected. All tests and alkyd resins were made with these fatty acids.

Comparison of ASTM Methods and Federal Test Method Standard Number 141. The iodine value and refractive index of each lot of fatty acids were determined according to ASTM method D555-54 (1). A sample of each fatty acid was then passed through a phthalic anhydride determination and a fatty acid separation according to ASTM method D1398-56T (2). The iodine value and refractive index of each separated acid fraction were determined by means of ASTM method D555-54 (1). Each determination was repeated according to Federal Test Method Standard Number 141 (3,4,5,).

Preparation of Alkyd Resins. Alkyd resins were processed in a 2-gal. stainless steel kettle equipped with an agitator. Each resin was prepared with an input of 52.6 parts of fatty acids, 21.7 parts of glycerol, and 33.1 parts of phthalic anhydride. All resins were solvent-processed in xylol. Approximately 4% of xylol, based on resin solids, was present in resins after processing. Two resins were prepared with each lot of fatty acids. One of these resins was processed at 400°F.; the other resin was processed at 450°F. After the processing temperature had been reached, a sample was removed from each resin each hour for a period of 9 hrs.

Analysis of Alkyd Resins. Preliminary analyses revealed that changes in iodine values and refractive indexes of fatty acids during alkyd resin processing were slight. Therefore only the samples removed at intervals of 2 hrs., 5 hrs., and 9 hrs. were analyzed. Each of the samples was saponified, the dipotassium salts were removed by filtration, and the fatty acids were separated according to ASTM method D1398-56T(2). Iodine values and refractive indexes of the separated fatty acids were determined by means of ASTM method D555-54.

Results and Discussion

Effects of Analysis. The results obtained by comparing ASTM and Federal methods of analyses are listed in Table I. No significant changes in either

TABLE I

Effects of Analysis on Iodine Value and Refractive Index

Fatty Acids	Iodine Value				Refractive Index at 25°C.			
	ASTM		Federal		ASTM		Federal	
	Initial	After analysis	Initial	After analysis	Initial	After analysis	Initial	After analysis
Linseed	177	176	177	173	1.4675	1.4688	1.4675	1.4693
Soya	139	139	141	138	1.4633	1.4640	1.4633	1.4636
Tall oil	132	129	131	131	1.4663	1.4649	1.4663	1.4665

TABLE II

Effects of Alkyd Resin Processing on Iodine Value and Refractive Index

Alkyd resin	Hours of processing	Iodine Value		Refractive Index at 25°C.	
		Resin processed at 400°F.	Resin processed at 450°F.	Resin processed at 400°F.	Resin processed at 450°F.
Linseed	2	170	174	1.4696	1.4700
	5	172	171	1.4693	1.4696
	9	172	168	1.4685	1.4695
Soya	2	141	137	1.4638	1.4645
	5	141	138	1.4637	1.4638
	9	135	137	1.4643	1.4639
Tall oil	2	126	124	1.4651	1.4665
	5	127	125	1.4650	1.4648
	9	126	125	1.4651	1.4649

iodine values or refractive indexes resulted from any analysis. Generally the analyses resulted in a slight decrease in iodine values and a slight increase in refractive indexes.

Effects of Alkyd Resin Processing. Iodine values and refractive indexes of the fatty acids separated from the alkyd resins are listed in Table II. Only minor changes in the iodine values and refractive indexes of the fatty acids resulted from the alkyd resin processing. Slightly more changes occurred in the linseed fatty acids and in the fatty acids from resins processed at 450°F. Decreases in iodine values were accompanied usually by increases in refractive indexes except for the tall oil acids. Decreases in iodine values of tall oil acids were accompanied generally by decreases in refractive indexes.

Acknowledgment

The authors wish to express their gratitude to the Resin Research Department for the preparation of the alkyd resins used in this investigation. They also acknowledge the helpful suggestions of C. A. Lucchesi and G. G. Schurr.

REFERENCES

1. Am. Soc. Testing Materials, Designation D555-54, "Standard Methods of Testing Drying Oils," 1954.
2. Am. Soc. Testing Materials, Designation D1398-56T, "Tentative Method of Test for Fatty Acid Content of Alkyd Resins and Resin Solutions," 1956.
3. Fed. Test Method Std. No. 141, Method No. 5061, "Iodine Number of Oils and Fatty Acids," 1958.
4. Fed. Test Method Std. No. 141, Method No. 4370, "Refractive Index," 1958.
5. Fed. Test Method Std. No. 141, Method No. 7031, "Oil Acids Content of Alkyd Resins," 1958.

[Received April 7, 1960]

Effect of Autoxidation Prior to Deodorization on Oxidative and Flavor Stability of Soybean Oil

C. D. EVANS, E. N. FRANKEL, PATRICIA M. COONEY, and HELEN A. MOSER,
Northern Regional Research Laboratory,[2] Peoria, Illinois

DEODORIZATION of vegetable oils is effective in removing volatile odor components and in destroying fat hydroperoxides (1,2,3,24). The effect of the hydroperoxide decomposition products on the subsequent oxidative stability of the oil is less well understood.

One effect of heating oxidized fats under deodorizer conditions is the formation of a reducing material that interferes with the Emmerie-Engel tocopherol determination (9). Fat hydroperoxides are known to undergo rapid destruction when the temperature is raised above 100°C. (7), and for this reason most workers (4,8,11,18,22,23) have used lower temperatures in both the oxidation and isolation procedures used to study products derived from fat autoxidation. However temperatures as high as 120°C. have been employed (13,21). O'Neill (17) and Williamson (25) studied the thermal decomposition of fat peroxides and purified methyl linoleate hydroperoxide at 100°C. Even after heating for 23 hrs., followed by molecular distillation at 110°C., Williamson found that a large amount of active peroxidic material remained in the distillate.

Chang *et al.* (5,6) concluded that oxidative polymers introduced into soybean oil during processing could serve as the precursors of flavor reversion compounds. Johnson *et al.* (15) studied the autoxidation of ethyl linoleate oxidative polymers and indicated that this reaction was a possible source of volatile flavor-reversion compounds in soybean oil. Holm *et al.* (14) have stated that high-molecular-weight carbonyl compounds, formed through the breakdown of oxidation products, were the substances responsible for poor oil stability and flavor reversion. They believed that the concentration of carbonyl compounds in a fat or oil was indicative of both the amount of oxidation that an oil has undergone and the future stability of a finished margarine. Some of these secondary

---

[1] Presented at fall meeting, American Oil Chemists' Society, October 20–22, 1958, Chicago, Ill.

[2] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.