64-68%, thus accounting for about 80% of the starting material. At 25-30° and 115-120°, yields of the above-mentioned products were low.

A mechanism is proposed which accounts for the formation of *trans*-9,10-epoxystearic acid from both oleic and elaidic acid autoxidized in the absence of solvent, and the consequent isolation of high-melting 9,10-dihydroxystearic acid when acetic acid is the solvent.

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The Effect of Extended Storage on the Properties of Tung Oil

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THE storage of tung oil for periods in excess of one year has been reported (2, 4, 5, 6, 7, 9, 10, 11) by several investigators. These reports are separable generally into two categories: a) small samples of oil stored under laboratory conditions with chemical and physical characteristics determined after varying periods of storage (5, 6, 7, 11); b) commercial quantities of oil stored under conditions that obtain in the trade, but with few or none of the characteristics of the stored oil reported (2, 4, 9, 10).

Some important points of agreement are evident in these investigations: a) storage containers should be either air-tight, or the exposed surface of the oil should be blanketed with an inert gas; b) storage containers should have a minimum of head space; c) authenticated instances of isomerization (accompanied without exception by extensive polymerization) are attributable to contamination of the oil during transportation, transfer, or storage. The contaminative material when identified invariably contains sulfur or iodine.

Because the oil storage problem is perennial in the domestic tung industry, a controlled storage experiment was designed with the purpose of gathering data that would support or negate some of the generalizations rife, (*i.e.*, stored oil isomerizes spontaneously, tung oil is difficult to store, etc.).

Experimental

Oil was stored in 1-gal. containers, tin-coated inside and closed with friction type (pressed in) lids, which for all practical purposes are air-tight. The tung oil used in the tests was taken directly after filtration at the mill in carefully cleaned and dry storage containers.

Three common storage conditions were simulated: a) unsheltered tank storage where containers were exposed to the direct rays of the sun throughout the day and to the prevailing atmospheric temperature the rest of the time; b) sheltered tank storage where samples were protected from the direct rays of the sun but exposed to the prevailing atmospheric temperature; c) indoor tank storage with reasonably constant temperature (20°-38°). Containers filled to within one-half inch of the top and others half-filled were stored under each condition for the purpose of determining the effect of head-space in the container. At the unsheltered location two sets of samples were stored, one set in containers painted a dull black, the other in containers coated with a highly reflective paint.

Examined on the practical basis of reproducibility in the hands of different analysts at widely spaced intervals of time, such commonly measured and reported characteristics for tung oil as iodine value, diene value, saponification value, unsaponifiable matter, etc., are of doubtful value. Under the conditions imposed by an extended storage experiment, index of refraction, gel time at 282°C., acid value, and viscosity are reliable, measurable with both accuracy and precision, and, considered collectively, quite adequate to characterize tung oil from the standpoint of quality. These measurements therefore were made at intervals over a three and one-half year period on the samples stored under various conditions. The official methods of the American Oil Chemists' Society (1) were used for refractive index (Method Ka 4-47), acid value (Method Ka 2-47), and viscosity (Method Ka 6-48); and the method of the American Society for Testing Materials (3) with modified equipment (13) for the gel time. Each stored sample was opened, and a sample of 24-40 ml. was withdrawn at each sampling. The refractive indices were determined at 5890 Å and 4358 Å (at 25°C.), but only the values determined at the former wave-length and the differences (dispersion) are tabulated. Results are given in Tables I and II.

Results and Discussion

The effects on tung oil of outdoor storage are surprisingly mild even though the tests were carried out in the southern part of the United States.

Storage containers with exterior coatings of a reflective paint show little, if any, superiority to their non-reflectively coated counterparts.

Tung oil in well-filled containers kept well throughout the three and one-half year period regardless of storage location and at the termination of the experiment, and met the A.S.T.M. specifications (3) for tung oil.

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TABLE I

Refractive Indices[1] and Dispersions[2] of Stored Tung Oil

Months stored	Unsheltered Storage Reflective Coating		Unsheltered Storage Non-reflective Coating		Sheltered Storage		Indoor Storage	
	Ref. Index N_D	Disp. $\times 10^4$	Ref. Index N_D	Disp. $\times 10^4$	Ref. Index N_D	Disp. $\times 10^4$	Ref. Index N_D	Disp. $\times 10^4$
Storage Containers Well Filled								
0	1.5174	280	1.5174	280	1.5174	280	1.5174	280
4	1.5178	280	1.5177	281	1.5177	281	1.5177	281
7	1.5180	281	1.5175	279	1.5179	280	1.5181	281
10	1.5178	279	1.5178	279	1.5179	280	1.5177	280
13	1.5176	278	1.5173	279	1.5176	280	1.5177	279
16	1.5178	279	1.5176	278	1.5179	280	1.5179	280
22	1.5178	279	1.5177	278	1.5180	280	1.5180	280
26	1.5180	277	1.5177	277	1.5181	280	1.5181	280
38	1.5180	278	1.5177	276	1.5182	278	1.5181	278
42	1.5175	278	1.5174	275	1.5179	278	1.5178	278
Storage Containers Half Filled								
0	1.5174	280	1.5174	280	1.5174	280	1.5174	280
4	1.5177	281	1.5177	280	1.5177	281	1.5177	281
7	1.5178	278	1.5176	279	1.5178	279	1.5179	280
10	1.5176	279	1.5176	279	1.5176	280	1.5176	279
13	1.5173	277	1.5173	277	1.5176	278	1.5174	278
16	1.5174	276	1.5174	276	1.5175	277	1.5175	276
22	1.5174	275	1.5174	275	1.5174	275	1.5174	272
26	1.5174	274	1.5174	275	1.5175	273	1.5173	272
38	1.5168	268	1.5171	271	1.5168	266	1.5166	262
42	1.5161	264	1.5167	271	1.5163	265	1.5155	261

[1] All refractive index measurements made at 25.0°C.
[2] Dispersion is reported as $(N_g - N_D) \times 10^4$ to simplify the work and because $(N_g - N_D)$ is so great in relation to the changes in density of the oil being examined.

Tung oil in the half-filled containers showed the deleterious effects of storage after one year as evidenced by the shortened heat test times, increases in viscosity, and small but probably insignificant decreases in the dispersions. At the end of 38 months some of the half-filled containers had a film of gelled oil over or around the edges of the oil surface. Partial polymerization, catalyzed by atmospheric oxygen present in the inordinate amount of head space above the oil in the half-filled containers, would explain all these changes as shown by Holmes and Pack (8).

Acid values showed a slight but definite increase throughout the storage tests, but in no case was the maximum value of 8.0 allowed by the A.S.T.M. specifications reached.

Although color measurements were not made, it was evident at the end of the storage experiment that the color of the oil in the half-filled containers was lighter than that in the full containers. The color of all the stored oil was very good at the time the tests were terminated.

All the stored oil samples were analyzed for the presence of *beta* (isomerized) tung oil by the method of O'Connor *et al.* (12) after storage for two years. No trace of the *beta* isomer (solid at room temperature when present in any significant quantity) could be detected in any of the samples at that time.

The accidental entry of moisture into some of the unsheltered containers caused a slight cloudiness of the stored tung oil. The cloudiness, apparent at the second examination period, persisted without worsening to the end of the experiment.

Summary

Tung oil has been stored in clean, well-filled gallon containers for more than three years and at the end of that time still met A.S.T.M. specifications.

TABLE II

Acid Values, Browne Heat Test Values, and Viscosities of Stored Tung Oil

Months Stored	Acid Values				Browne Heat Tests, minutes				Viscosities, stokes at 25°C.			
	Unsheltered		Shelt.	Indoor	Unsheltered		Shelt.	Indoor	Unsheltered		Shelt.	Indoor
	Reflec. coat.	Non-reflec. coat.			Reflec. coat.	Non-reflec. coat.			Reflec. coat.	Non-reflec. coat.		
Storage Containers Well Filled												
0	1.63	1.63	1.63	1.63	11.50	11.50	11.50	11.50	2.00	2.00	2.00	2.00
4	1.63	1.63	1.63	1.63	11.50	11.50	11.50	11.50	2.00	2.00	2.00	2.00
7	1.75	1.92	1.75	1.75	11.42	11.00	11.50	11.50	2.25	2.25	2.00	2.00
10	2.04	1.86	1.92	1.92	11.00	11.67	12.00	11.83	2.25	2.25	2.25	2.25
13	1.98	2.15	1.92	2.00	11.42	11.17	11.92	11.83	2.25	2.25	2.25	2.25
16	2.27	2.33	2.04	2.10	11.25	11.00	11.75	11.75	2.50	2.50	2.25	2.25
22	2.74	3.14	2.38	2.50	11.00	10.83	11.42	11.42	2.50	2.50	2.25	2.25
26	2.47	2.96	2.33	2.47	11.17	10.67	11.33	11.25	2.25	2.50	2.25	2.25
38	3.22	3.88	2.46	2.55	11.17	11.00	11.50	11.17	2.25	2.50	2.25	2.25
42	3.42	4.15	2.23	2.39	11.50	11.08	11.90	11.57	2.75	2.75	2.50	2.75
Storage Containers Half Full												
0	1.63	1.63	1.63	1.63	11.50	11.50	11.50	11.50	2.00	2.00	2.00	2.00
4	1.63	1.63	1.63	1.63	11.25	11.00	11.50	11.50	2.00	2.00	2.00	2.00
7	1.75	1.92	1.75	1.75	10.83	10.83	11.00	10.75	2.50	2.50	2.25	2.25
10	1.92	1.86	1.92	1.92	10.58	10.75	11.00	11.25	2.50	2.25	2.25	2.25
13	2.04	2.04	1.92	1.92	10.25	10.50	10.67	10.50	2.50	2.50	2.50	2.50
16	2.10	2.21	1.86	1.92	10.00	10.25	10.00	10.00	2.75	2.75	2.50	2.75
22	2.68	2.86	2.22	2.32	9.50	10.00	9.00	9.00	3.20	2.75	3.00	3.20
26	2.47	2.86	2.28	2.37	9.33	9.50	8.75	8.50	3.00	3.00	3.00	3.40
38	3.26	3.74	2.18	2.36	7.67	9.25	7.42	6.83	3.00	3.00	3.00	3.40
42	3.60	4.01	2.10	2.37	7.50	9.10	7.17	6.20	6.27	4.35	8.84	12.90

Storage locale (indoor, outdoor, sheltered, or unsheltered containers) and the exterior coating on the containers in exposed locations were found to be of less importance than protection of the stored oil from atmospheric oxygen.

The most pronounced effect of prolonged storage on tung oil is a shortening of the heat test (gel time at 282°C.).

Uncontaminated tung oil does not spontaneously isomerize during storage.

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A Quick Dilatometric Method for Control and Study of Plastic Fats

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DILATOMETRY has been widely used for studying phase change. Its use on fats was apparently first reported by Normann,[1] and a detailed study of many fats and fat mixtures has been described by Hofgaard.[2] Various types of equipment and modes of application have been recommended. Bailey[3] has contributed to design and use of the method and has reviewed developments in some detail.[4] A particularly interesting discussion of dilatometry as applied to margarine is that of Andersen.[5]

For several years dilatometry has been employed in our research laboratories for fundamental study of fat phase behavior and in our factory control laboratories for plant hydrogenation control. An apparatus of considerable convenience, and its method of application to control procedures are described here. With the equipment here described, results of good reproducibility are obtained within two hours.

The dilatometers used in this work are of the volumetric type, in which the fat sample in a glass bulb expands against a confining liquid (mercury), free to move in a glass capillary. By measuring the changes in length of the mercury column, the volume changes can be calculated for the fat sample. It is necessary only to know the fat weight and the capillary calibration for the instrument. No stem correction for exposed capillary is necessary. The effects of mercury and glass expansion are eliminated by the process of taking "liquid" readings. The final determined value is put in terms of "solid content" as deduced from the rather general principle that complete solidification of most fats involves a change of 10% in specific volume upon total solidification — or 0.1% change upon 1% solidification. Details are presented later.

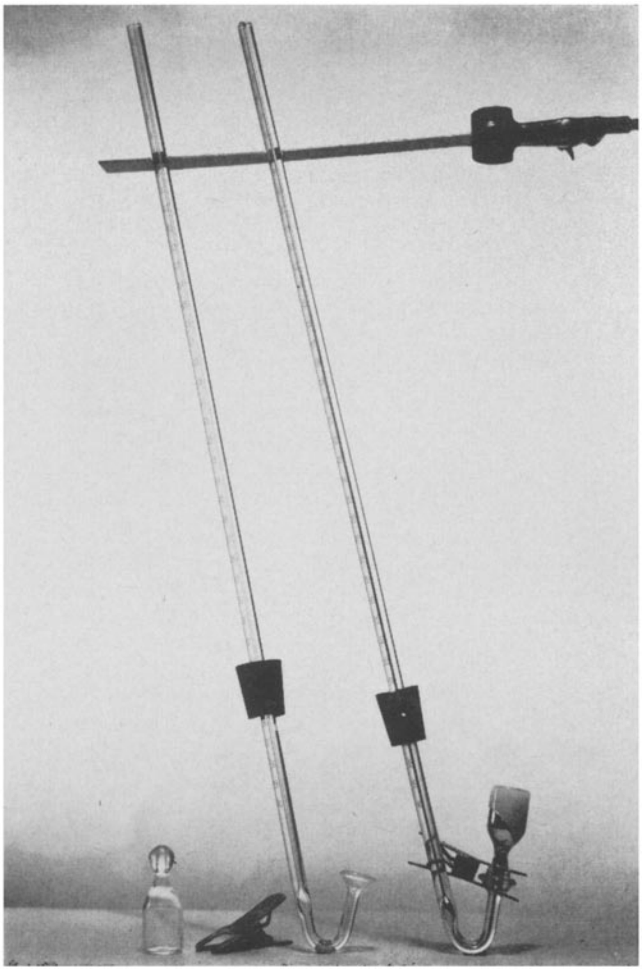

FIG. 1. Picture of unassembled and assembled filled dilatometers.

Apparatus

A picture of the dilatometer is given in Figure 1. The glass capillary as shown in the picture was of