TABLE V

Comparison of Plasticizing Efficiency of Selected Acetylated TOFA-Formaldehyde Esters

	Tensile, psi	100% Modulus	% Elongation	Hardness (15 sec)	Brittle pt., °C	Volatility (11 days)	Hexane ext. (3 days)	Mineral oil ext. (10 days)	Soapy water ext. (7 days)	Heat stability, min	Light stability, hr
Esters of polymeric condensates (degree of —C=C—saturation)											
Methyl TOFA-formaldehyde (95%)	3190	1930	340	76	−10	2.3	4.65	0.61	2.0	60	456
Ethyl TOFA-formaldehyde (89%)	2610	1200	360	84	−28	3.3	11.2	2.2	2.6	60	144
Ethyl TOFA-formaldehyde (95%)	3150	1930	360	81	−10	1.7	5.75	0.85	1.4	60	340
Isopropyl TOFA-formaldehyde (69%)	2730	1750	340	91	−31	3.0	17.2	4.1	4.1	60	.....
n-Propyl TOFA-formaldehyde (69%)	2085	842	370	84	−32	2.8	14.0	3.3	1.9	90	144
n-Propyl TOFA-formaldehyde (95%)	3010	1970	275	80	−9	1.1	5.60	0.52	1.4	90	483
THF TOFA-formaldehyde (90%)	3070	2050	280	81	−4	1.1	1.17	0.39	2.3	90	166
Esters of monomeric condensates (degree of —C=C—saturation)											
Ethyl aromatized TOFA-formaldehyde (99%)	3040	1415	360	66	−30	5.1	13.1	4.4	2.4	90	.....
n-Propyl TOFA-formaldehyde (93%)[a]	3400	1970	345	78	−12	1.8	4.15	2.3	0.6	60	.....
n-Propyl TOFA-formaldehyde (92%)	2905	1475	340	74	−24	2.3	6.60	1.1	2.3	90	396
THF TOFA-formaldehyde (85%)	3220	1580	350	78	−42	3.3	12.75	7.1	3.0	90	117
DOP	2680	1400	345	77	−31	3.30	13.0	2.48	0.68	120	>500
S409	3020	1901	340	86	−13	0.64	4.9	2.90	0.90		>600

[a] Crude prod.

hydroxyl groups and leading exclusively to 1,3-dioxane ring formation.

In the best experiment, the ethyl ester of TOFA ($bp_{0.4}$ 152–157C; S.V., 178.2; A.V., 1.8; I.V., 112.2) was stirred for eight hr at 70C with 0.33 part trioxane and 0.15 part anhydrous ferric chloride. The reaction mixture was dissolved in heptane, filtered and washed with water to remove ferric ion and excess formaldehyde. The heptane was distilled to obtain 1.10 parts of a yellow oil.

Anal. Calc'd for addn. of 2 HCHO to —C=C—: S.V., 153.8; A.V., 0.0; I.V., 0.0; OH.V., 0.0. Found: S.V., 173.8; A.V., 10.3; I.V., 38.9; OH.V., 0.19.

The data on this crude product indicate ca. 61% saturation of double bonds with only ca. 3% conversion to hydroxyl-containing derivatives and 5% cleavage of ester groups. The active hydrogens required for these side reactions were derived, presumably, from the water wash.

The similar use of 100% H_2SO_4 and boron fluoride as condensation catalysts instead of ferric chloride were less satisfactory. The degrees of double bond saturation were lower and the side reactions were not avoided. Ferric chloride, or possibly other weak Lewis acids, would thus appear to be the catalysts of choice for future development work along this line.

REFERENCES

1. Arundale, E., and L. A. Mikeska, Chem. Rev. *51*, 505 (1952).
2. Case. E. (Sinclair Refining Co.), U.S. 2,895,974 (1959).
3. Floyd, D. E., R. F. Paschke, D. H. Wheeler and W. S. Baldwin, JAOCS *33*, 609 (1956).
4. Fokin, S., J. Russ. Chem. Soc. *43*, 809; C.A. *6*, 477 (1912).
5. Pigulevsky, G. V., and M. G. Tatarskaya, J. Gen. Chem. USSR (Eng. Trans.) *20*, 1517 (1950).
6. Rockett, J. (Arnold, Hoffman & Co., Inc.), U.S. 2,764,604 (1956).
7. Roe, E., and D. Swern, Eastern Reginal Lab., USDA, unpublished data.
8. Rössner, H., and W. Cotton, (Hochst a/M), U.S. 988,032 (1911).
9. Waldmann, H., and W. Stein, (Henkel and Cie, G.M.b.H.), Ger. 1,054,444 (1959).

[Received June 9, 1964—Accepted October 20, 1964]

A Study of the Influence of Storing Wood on the Yield and Quality of Tall Oil

WALTER COWART and D. C. TATE, Champion Papers, Inc., Canton, North Carolina, and JOHN CHURCHILL, Champion Papers, Inc., Hamilton Ohio

Abstract

In 12 weeks of storage time pine roundwood lost approximately 11% in tall oil yield, while for the same length of time purchased slabwood chips (pine) lost 64%. Most of the loss in yield occurred within six weeks. The purchased chips lost more tall oil yield in one week than the roundwood in 12 weeks.

The loss in yield from the roundwood was due entirely to the loss in yield of fatty acids. The loss in yield in the purchased slabwood chips was due predominantly to the loss in yield in fatty acids; however, there was, in addition, a small loss in resin acids, and a very small loss in unsaponifiables.

As for tall oil quality, by the end of 12 weeks of storage the acid number of tall oil from both roundwood and purchased chips had dropped below 160.

In correlating the yield of tall oil from the wood extractions with the yield of tall oil from the black liquor from digester cooks, it appears that on the average about 80% to 88% of the extracted tall oil can be found in the black liquor.

Introduction

IN AN EFFORT to insure maximum possible tall oil production, a laboratory fact-finding program was initiated to secure more information and data concerning the fluctuations in tall oil production and the reasons behind these fluctuations. The study of age vs. tall oil yield for roundwood and purchased slabwood chips was a part of this overall program. Other aspects of this program, to be covered in additional reports, are the solvent extractions of weekly composites of wood to the digesters, the weekly determinations of tall oil potential to the smelters and the waste treatment plant, and the study of the effect of mixing hardwood and pine liquors on tall oil recoveries.

It is important to have the above data in order to determine how much tall oil is available, how

TABLE I
Tall Oil Aging Study
Comparison of Tall Oil Yield and Quality with Wood Storage Time
Basis Saponified Trichloroethane Extract of Wood Chips—Carolina

Date	Wood Storage Time	% Loss in Tall Oil Yield	Yield—% on OD Wood				Sap. No.	Acid No.	% Rosin Acids	(By Diff.) % Fatty Acids	% Unsaps	Tall* Oil Yield lb/Ton AD Pulp
			Tall Oil	Rosin Acids	Fatty Acids	Unsaps						
Roundwood												
7/19/63	Fresh	0	2.89	1.05	1.56	0.28	183	167	36.3	54.1	9.6	123.8
8/ 9/63	3 wk	1.7	2.84	1.14	1.43	0.27	172	161	40.3	50.4	9.3	121.7
8/30/63	6 wk	14.9	2.46	0.92	1.30	0.24	174	165	37.3	52.9	9.8	105.4
10/11/63	12 wk	7.3	2.68	1.09	1.30	0.29	171	157	40.6	48.5	10.9	114.8
Purchased Slabwood Chips												
7/26/63	Fresh	0	3.09	1.24	1.63	0.22	191	172	40.0	52.9	7.1	132.4
8/ 2/63	1 wk	17.5	2.55	1.13	1.26	0.16	184	177	44.2	49.5	6.3	109.3
8/16/63	3 wk	33.7	2.05	1.05	0.84	0.16	180	169	51.1	41.2	7.7	87.8
9/ 6/63	6 wk	56.6	1.34	0.83	0.39	0.12	170	163	61.7	29.4	8.9	57.4
10/18/63	12 wk	64.4	1.10	0.67	0.32	0.11	189	156	61.4	28.8	9.8	47.1
Regular Mill Chip Pile												
7/ 3/63	Approx. 8 wk	—	1.45	—	—	—	—	—	—	—	—	62.1
10/19/63	14 wk	—	1.06	0.61	0.30	0.15	185	147	57.5	28.5	14.0	45.4

* The conversion from % on O. D. wood to No./ton A. D. pine pulp is based on a pulp yield of 42% or that 4285. lbs. O. D. wood equal one ton A. D. pulp.

much of the available is being collected, and whether the losses that are occurring can be prevented.

The aging study, showing the effect of aging on the yield as well as on the quality of tall oil, was carried out on a small scale. Limited by the number of people and amount of time and equipment available, it was not possible to deal with a large quantity of roundwood or chips, or to go into a large amount of detail as to different species or different seasons of the year for aging. Some of these points may be examined later. Likewise, time did not permit the study of the effect of aging on turpentine yield. There are still several points that are not clearly explained by the data, as will be observed on reading this report. These unusual results may be explained whenever further work is possible.

Since the actual aging of the roundwood and purchased chips was to be carried out at Carolina, it was decided to use solvent extractions as laboratory pulping facilities were not available at Carolina. However, before starting the aging study it was necessary first to develop a satisfactory procedure for solvent extraction of wood to determine tall oil yield. The technical details of this procedure will be covered in a separate report.

The attempt to correlate solvent extract and pulped yield of tall oil, in black liquor, was done at Knightsbridge in the pulp laboratory. One of the purposes of the weekly solvent extractions at Carolina is to establish the same correlation between solvent extract and pulped yield of tall oil over the different seasons of the year.

Experimental Procedures and Data

Roundwood

Four short-leaf pine trees were taken on July 18, 1963, from Duke Power Company land, Morganton District, in the Lake James area. The trees were all approximately the same size averaging 11.5 in. in diameter. They varied from 12 to 13 in. in diameter at the bottom to 8.5 to 9 in. in diameter at the top, or last bolt taken from the trees.

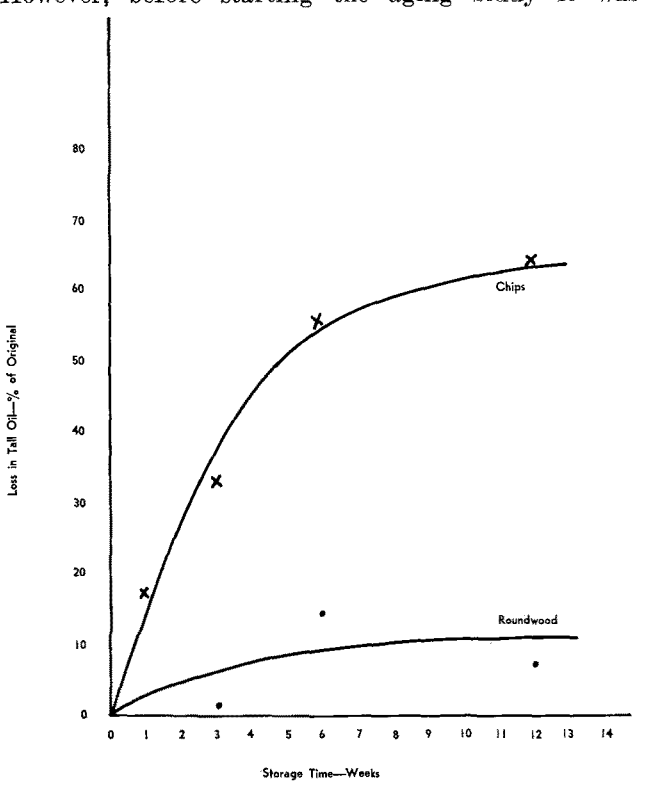

FIG. 1. Purchased Chips and Roundwood Percentage Loss in Tall Oil Yield vs. Storage Time.

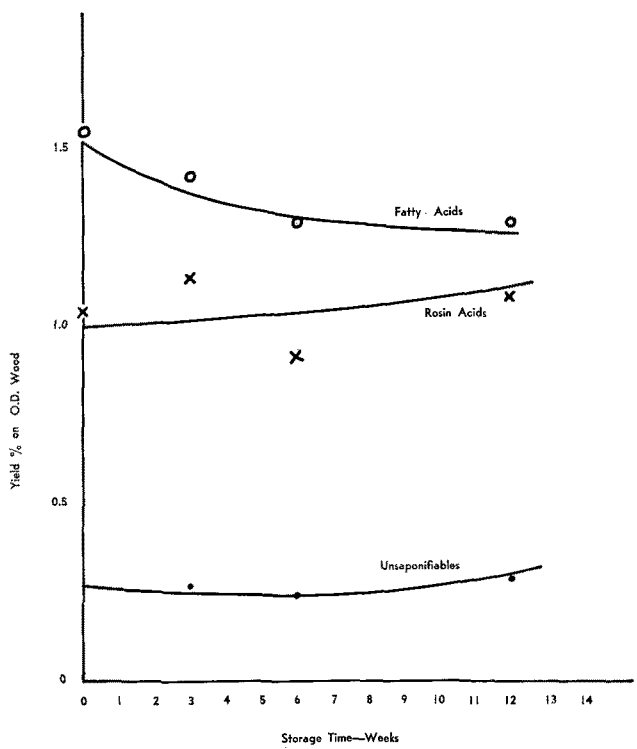

FIG. 2. Roundwood Yield of Rosin and Fatty Acids and Unsaponifiables vs. Storage Time.

Each tree was cut into six 5-ft-long logs. These logs were transported to Carolina immediately after harvesting and labeling. The four top and four butt logs were used in determining the difference between fresh-cut butt and top logs in tall oil content. The remaining logs were used in the aging study and were stored on the wood yard. Four age intervals were used: fresh cut, 3 weeks, 6 weeks, and 12 weeks. Each storage interval was tested on chips made from a composite of one log from each of the four trees, representing different heights in the tree. Before being chipped on one of the mill chippers, the logs were barked by hand. Afterwards, a representative sample of the chips was taken to the laboratory for solvent extraction and another sent to Knightsbridge for pulping.

Purchased Slabwood Chips

Purchased chips were obtained from the Gilkey Lumber Company on July 25, 1963. The chips were made from fresh slabwood from trees cut in the same area as the four pine trees mentioned above. The chips were obtained on the Carolina Wood Yard in a pile that measured 12.5 ft × 14.5 ft × 4 ft high. The pile contained 5,920 lb of chips. Five age intervals were used; fresh cut, 1 week, 3 weeks, 6 weeks, and 12 weeks. The samples for solvent extraction and pulping were always taken from about the center of the pile and at least halfway down into the pile.

Tall Oil from Solvent Extractions: Carolina

The chips were reduced to matchstick size in a Wiley Mill and then spread out to air dry in the laboratory for two days. The air-dried matchsticks were ground in a Wiley Mill to pass a screen with 1 mm diam opening. The moisture content of the sawdust was determined by drying 200 AD g overnight in an oven at 105C. Using a soxhlet unit, 400 AD g of sawdust were extracted for 18 hr with 1, 1, 2 trichoroethane. The sawdust was allowed to soak overnight in the solvent before and halfway through the extraction period. Following extraction the extract was concentrated first at atmospheric conditions and finally under vacuum. The concentrated extract was saponified by refluxing for 6 hr with 100 cc of 2 *N* alcoholic KOH, and then made up to 2 liters with distilled water. Aliquots were acidified 4 *N* H_2SO_4 and ether extracted with ethyl ether. Tests were run on the ether extracted material according to ASTM methods. Tall oil yield was determined from the weight of the ether extract and based on the OD weight of the wood extracted. [Note 1) The conversion from percent on OD wood to lb/ton AD pulp is based on a pulp yield of 42% or that 4.285 lb OD wood equals one ton AD pulp. Note 2) Trichloroethane for wood extractions, and petroleum ether for Buckeye test.]

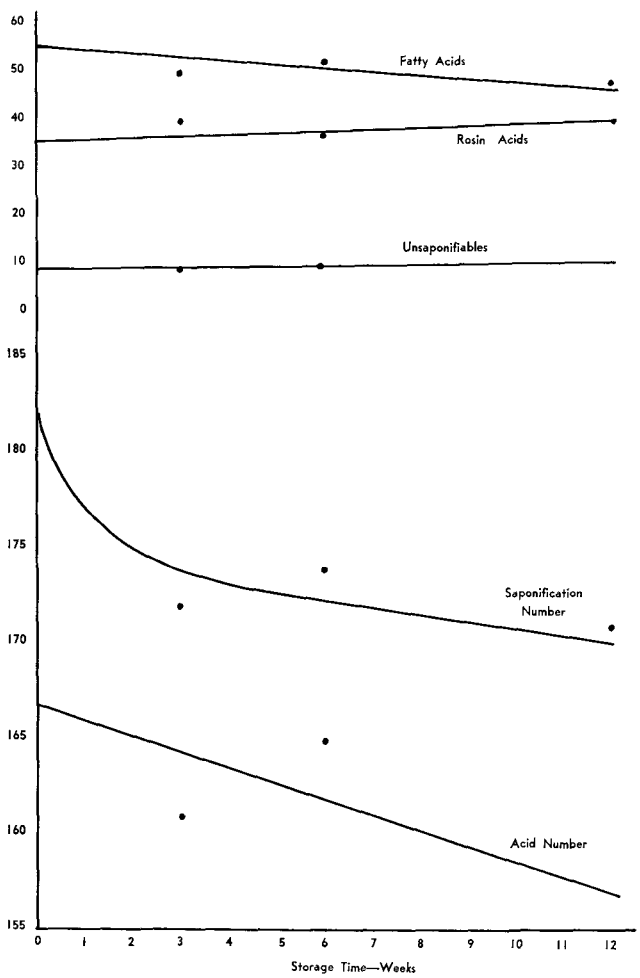

FIG. 3. Roundwood Tall Oil Quality vs. Storage Time.

Tall Oil from Digester Cooks: Knightsbridge

Part of the chip sample was cooked in a stationary indirectly-heated digester to a 16 PN. A charge of 2,000 OD g of full-sized chips was used. All of the black liquor was collected by thoroughly washing the pulp and a Buckeye test was run on the total collected liquor. The yield of tall oil was figured on a liquor solids basis and back-calculated to a wood basis knowing the total wood charged and the total solids in the black liquor.

The other part of the chip sample was extracted with trichloroethane using a procedure similar to that used at Carolina. However, the extraction results obtained were not used in the aging study due to the shipping time involved.

Results

Roundwood Aging Study—Carolina (Table I)

The loss of tall oil yield over the 12-week aging period was very small, approximately 11% (Fig. 1.). The yield, based on OD wood, decreased from 2.9% to about 2.6% or from 124 lb tall oil per ton AD pulp Note 1 to about 110 lb/ton. This is taking into consideration that for some unexplained reason the yield was less at the end of 6 weeks than at the end of 12 weeks. However, the yield of tall oil from the fresh wood was somewhat lower than normally experienced. For comparison, the tall oil yield from the extractions of weekly composites of wood to the digesters for August through December 1963 averaged 3.4% or 144 lb/ton.

The yield of fatty acids over the 12 weeks decreased from 1.6% to 1.3%; while the yields of rosin acids and unsaponifiables increased only very slightly (Fig. 2), from 1.05% to 1.09% and from 0.28% to 0.29%, respectively.

As for the quality of the tall oil over the aging period, (Fig. 3) the saponification number, the acid number, and the per cent fatty acids decreased in value; the per cent rosin acids and the per cent unsaponifiables increased. The saponification number decreased from 183 to 171, the acid number from 167 to 157, and the per cent fatty acids from 54.1

TABLE II

Comparison of Tall Oil from Different Heights of a Fresh-Cut *Pine* Tree Basis Saponified Trichloroethane Extract of Wood Chips—Carolina

Section of Tree	Yield—% on OD Wood				Sap. No.	Acid No.	% Rosin Acids	(By Diff.) % Fatty Acids	% Unsaps.	Tall Oil Yield lb/Ton AD Pulp
	Tall Oil	Rosin Acids	Fatty Acids	Unsaps						
Tops	3.2	0.99	1.85	0.36	180	159	30.8	57.9	11.3	137.1
Middle	2.9	1.05	1.57	0.28	183	167	36.3	54.1	9.6	124.3
Butts	2.9	1.02	1.61	0.27	186	168	35.2	55.6	9.2	124.3

to 48.5. The percent rosin acids increased from 36.3 to 40.6, and the per cent unsaponifiables from 9.6 to 10.9.

Tall Oil from Different Heights in Fresh-Cut Trees—Carolina (Table II, Fig. 4)

The tops of the fresh-cut pine trees produced a higher tall oil yield than did the middle and butt sections. The tops yielded 3.2% or 137 lb/ton and the middle and butts 2.9% or 124 lb/ton.

The larger tall oil yield of the top sections was due to a larger yield of fatty acids and unsaponifiables. The tops had a yield of fatty acids of 1.85% as against 1.57% and 1.61% for the middle and butt sections, respectively; a yield of unsaponifiables of 0.36% as against 0.28% and 0.27%; and a yield of rosin acids of 0.99% as against 1.05% and 1.02%.

The top sections, in comparison with the middle and butt sections, which were about the same, had a lower saponification number, acid number and per cent rosin acids, and a higher per cent fatty acids and per cent unsaponifiables. The tops had a saponification number of 180 as compared to 183 and 186 for the middle and butt sections, respectively; an acid number of 159 as compared to 167 and 168; a per cent rosin acids of 30.8 as to 36.3 and 35.2; a per cent fatty acids of 57.9 as to 54.1 and 55.6 and a per cent unsaponifiables of 11.3 as to 9.6 and 9.2.

Purchased Slabwood Chips Aging Study—Carolina (Table I)

The loss of tall oil yield over the 12-week aging period was a dramatic 64%. One fourth of this total loss occurred within one week, one half by three weeks and seven eighths by six weeks, indicating a very sharp drop-off at first and then a gradual leveling off. The yield, based on OD wood, decreased from 3.1% all the way down to 1.1% or from 132 lb tall oil/ton A.D. pulp down to 47 lb/ton. Within one week the tall oil yield had dropped to 2.6% or 109 lb/ton; by three weeks to 2.1% or 88 lb/ton; and by six weeks to 1.3% or 57 lb/ton.

The yield of fatty acids over the 12 weeks decreased sharply, as did the total yield, from 1.63% to 0.32% (Fig. 5). The yield of rosin acids decreased also, but more gradually, from 1.24% to 0.67%. The yield of unsaponifiables decreased even more gradually from 0.22% to 0.11%. However, most of the losses in the above yields had occurred by six weeks. As shown in Figure 5 the fresh wood contained a greater yield of fatty acids than rosin acids. Within two weeks the yields were approximately the same, and afterwards the yield of fatty acids fell off below that of the rosin acids.

As for the quality of the tall oil over the 12-week aging period (Fig. 6), the saponification number, the acid number, and the per cent fatty acids decreased in value; the per cent rosin acids and per cent unsaponifiables increased in value. These changes were more pronounced than for the roundwood in keeping with the greater loss in yield. The high saponification number for the 12-week sample cannot be explained; however, as will be discussed later, the saponification number for the 14-week regular mill chip pile sample was also high. The saponification number decreased from 191 to 170 (six weeks), the acid number from 172 to 156, and the per cent fatty acids from 52.9 to 28.8. The per cent rosin acids increased from 40.0 to 61.4, and the per cent unsaponifiables from 7.1 to 9.8.

Regular Mill Chip Pile—Carolina

The regular mill purchased chip pile was sampled

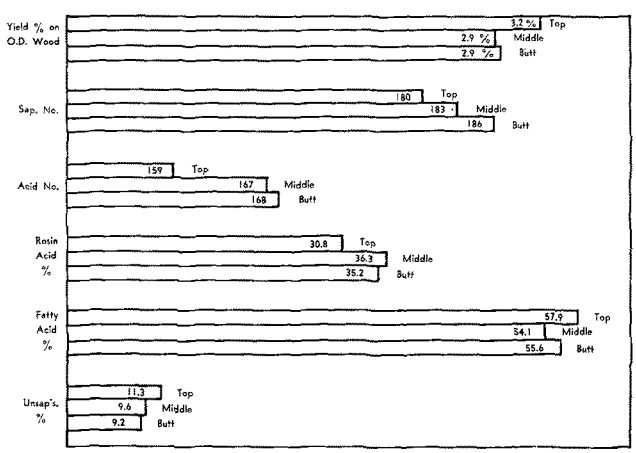

FIG. 4. Comparison of Tall Oil from Different Heights of a Fresh Cut Pine Tree.

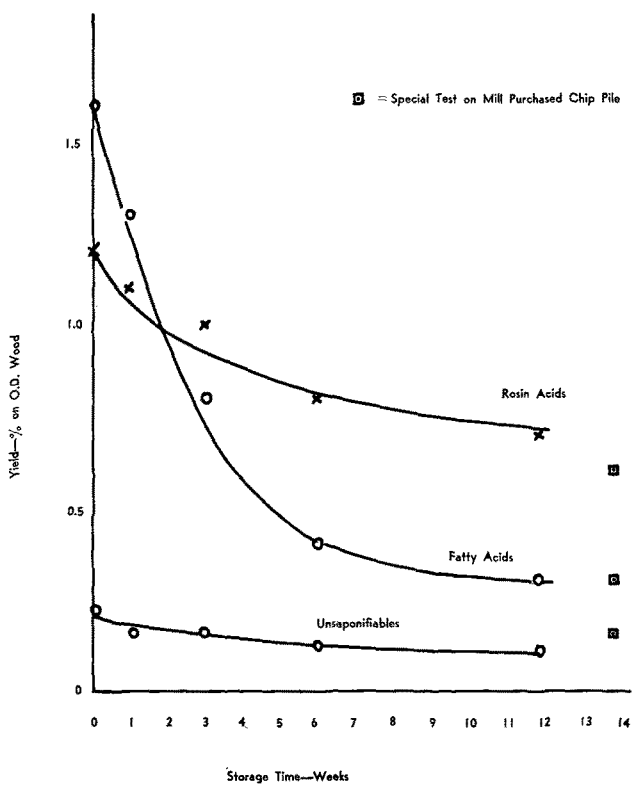

FIG. 5. Purchased Chips Yield of Rosin and Fatty Acids and Unsaponifiables vs. Storage Time.

TABLE III

Comparison of Tall Oil Yield from Wood with Tall Oil Yield after Pulping Basis Saponified Trichloroethane Extract of Wood Chips and Buckeye Test on Black Liquor from Digester Cooks—Knightsbridge

Wood Storage Time	Trichloro. Extract Tall Oil Yield % on OD Wood	Black Liquor Tall Oil Yield % on OD Wood	% Yield from Black Liquor to Yield from Extract
Roundwood			
Fresh	2.70	2.17	81%
3 wk	2.54	1.93	76
6 wk	2.50	1.95	78
12 wk	2.46	2.00	81
			Av. 79.0%
Purchased Chips			
Fresh	2.84	2.97	100+ %
1 wk	2.10	1.61	76
3 wk	1.99	1.51	76
6 wk	1.70	1.08	64
12 wk	1.12	1.01	92
			Av. 81.6%

Carolina Special Weekly Tall Oil Potential Tests

August Through December	Extracted Tall Oil Yield from Weekly Composites of Wood to Digesters	Total Tall Oil Potential: Production and Losses to Smelters and Waste Treat. Plant
1963	143.8 lb Tall Oil/ Ton AD Pulp	126.2 lb/Ton 87.7%

at the beginning and ending of the aging study. At the first sampling the pile contained about 470 cords and represented an approximate storage time of eight weeks. At the last sampling the pile held about 1500 cords and represented an approximate storage time of 14 weeks. Before any chips had been removed and sent to the pulp mill, the pile measured 190 ft x 180 ft x 30 ft high with tapered sides and contained about 2200 cords. The 14-week sample was taken at about the center of the pile and at a depth of about 24 ft.

As shown in Table I and Figures 5, and 6, the good agreement between the special aging study and the regular mill chip pile samples indicate that the small experimental chip pile simulated the regular storage conditions quite well.

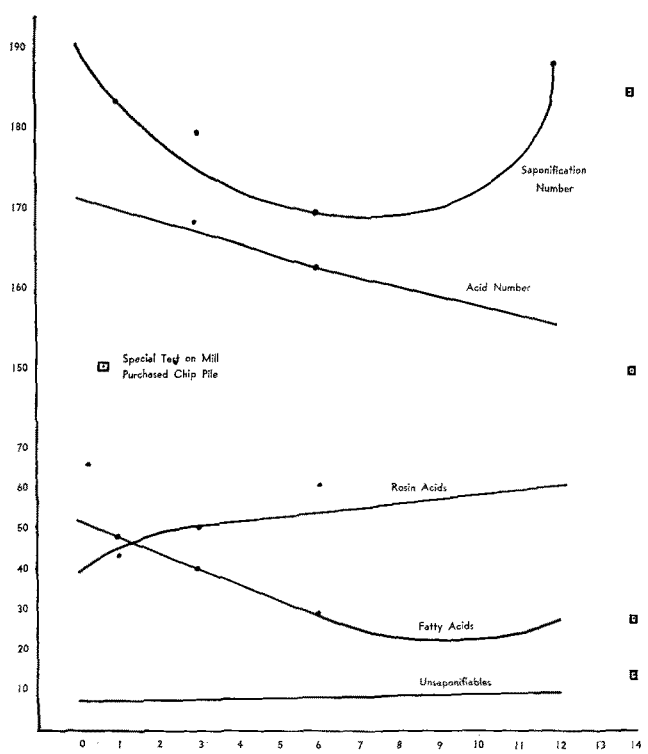

FIG. 6. Purchased Chips Tall Oil Quality vs. Storage Time.

Extracted Yield vs. Pulped Yield—Knightsbridge (Table III, Fig. 7)

The attempt to correlate the yield of tall oil from the wood extractions with the yield of tall oil from the black liquor from digester cooks has produced results that have not been completely conclusive. But it does appear that about 80% of the extracted tall oil can be found in the black liquor. There are some wide swings away from this value, primarily with the purchased chips, and these have not been satisfactorily explained at this time. Also, unexplained is the reason for the loss in tall oil yield on pulping as compared to the extracting of wood. It is not known whether it is because that two different solvents Note 2 were used, or that some of the material was actually lost on pulping. It is hoped to be able to resolve these questions with additional laboratory studies that are planned.

The Carolina special weekly tall oil potential tests give general support to the above mentioned 80% figure. For the five months, August through December 1963, the total tall oil potential averaged 126 lb tall oil per ton AD pulp. This consisted of tall oil production, and tall oil loss to smelters and waste treatment plant. For the same period the tall oil yields from the extractions of weekly composites of wood to the digesters averaged 144 lb/ton. Therefore, the relationship between solvent extract and pulped yield of tall oil gives a comparative figure of 88%

Conclusions

In 12 weeks of storage time the roundwood lost approximately 11% in tall oil yield while for the same length of time the purchased chips lost 64%. Most of this loss in tall oil yield occurred within six weeks.

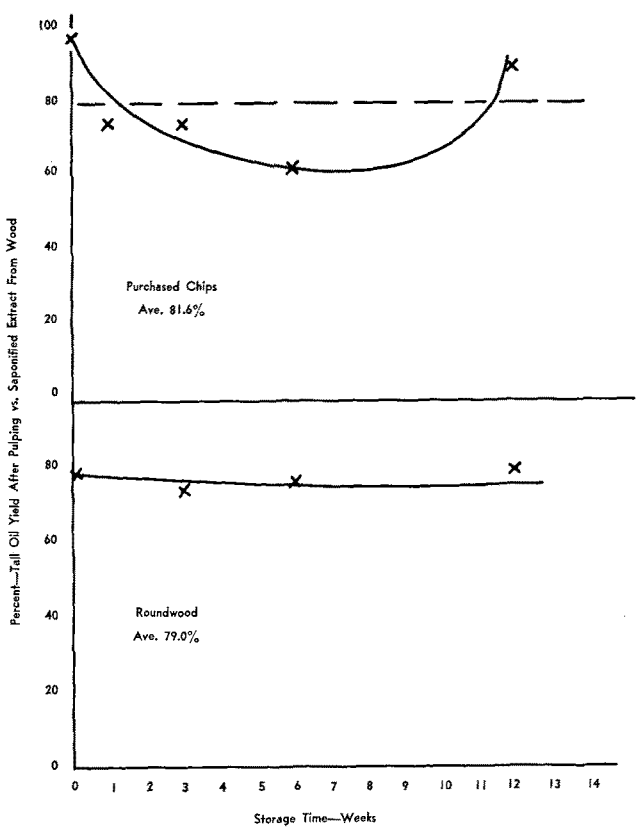

FIG. 7. Tall Oil Yield from Wood after Pulping.

For the purchased chips one half of the total loss in tall oil occurred within three weeks of storage. In fact the purchased chips lost more tall oil yield in one week than the roundwood in 12 weeks.

As far as tall oil yield is concerned, assuming a constant volume of chips in storage, there would be less sales revenue lost over a year's time by rotating the chip pile every six weeks than every week. This is due to the faster rate of tall oil loss in the first weeks of storage. It would be even more economical to leave the chips stored for longer periods, not exceeding the point at which pulp quality and yield would be affected. By accepting the loss of tall oil in this chip pile, a continuing loss at the faster initial rate would be prevented in the chips that otherwise would be rotated on a one to six weeks' basis.

As for tall oil quality, by the end of 12 weeks of storage the acid number of tall oil from both roundwood and purchased chips had dropped below the minimum specification of 160. This specification was set by Chemicals Division for Champion's Crude Dehydrated Tall Oil.

The loss in yield in the roundwood was due entirely to the loss in yield of fatty acids. The loss in yield in the purchased chips was due predominantly to the loss in yield in fatty acids; however, there was in addition a smaller loss in rosin acids, and a very small loss in unsaponifiables.

The loss in tall oil yield in the experimental purchased chip pile was substantiated by the loss in tall oil yield in the regular mill purchased chip pile.

In comparing the tall oil from the top sections of trees with the middle and butt sections, which were very similar, the tops had a little more yield, but a little poorer quality tall oil than the middle and butt sections; however, the differences were not too significant.

In attempting to correlate the yield of tall oil from the wood extractions with the yield of tall oil from the black liquor from digester cooks, it appears that on the average about 80% to 88% of the extracted tall oil can be found in the black liquor. The loss in tall oil yield on pulping as compared to the extracting of wood is unexplained at this time.

ACKNOWLEDGMENT

The assistance of T. L. Clark and C. D. Harkins of the Carolina Division Laboratory and personnel of Carolina Division Wood Procurement Office is gratefully acknowledged.

[Received May 6, 1964—Accepted December 28, 1964]