# LIST OF REFERENCES TO THE LITERATURE ON TALL OIL

(Tallol, Liquid Rosin, Pine oil, or Black Liquor Soap)

(Report)





UNITED STATES DEPARTMENT OF AGRICULTURE
FOREST SERVICE
FOREST PRODUCTS LABORATORY
Madison, Wisconsin
In Cooperation with the University of Wisconsin
Revised, August 1938

## LIST OF REFERENCES TO THE LITERATURE ON TALL OIL (TALLOL, LIQUID ROSIN, PINE OIL OR BLACK LIQUOR SOAP)

By

M. W. Bray, Senior Chemist
J. S. Martin, Associate Engineer
and
L. H. Smith, Research Fellow, Victoria, Australia

Revised August 1938

- 1. P. Klason, Tek. Tid. 23, 31(1893).
- 2. E. Larson, Svensk. Kem. Tid. 17, 148 (1905).
- 3. H. Bergstrom and O. Fagerlund, Jernkontorets Ann. Bihaug. 2, 575, 649 (1908).
- 4. W. Fehrion, Z. Angew. Chem. 22, 582 (1909).
- 5. H. Bergstrom, ibid 11, 297 (1910); ibid 12, 507 (1911).
- 6. Pine oil obtained in the manufacture of soda cellulose by Hilding Bergstrom. Papier-Fabricant 9, Fest. Auslandschieft 76-82, C.A. 6, 421 (1912).
- 7. H. Bergstrom, Papier-Fabr. 11, (25) 730 (June 20, 1913).
- 8. C. G. Schwalbe, Chem. Ztg. 38, 926 (1914).
- 9. Constituents of colophony and sulphate black liquor by 0. Ashan.

  Ber. 45: 867-86 (1921); abst. J.S.C.I. 40 (12):439A (June 30, 1921);

  abst. Paper Trade J. 73 (25): 54 (Dec. 22, 1921).
- 10. Some experiments on the separation of fatty acids and resin acids in the liquid resin from sulphate pulping process by Astrid Cleve von Euler. Arkiv. Kemi. Mineral Geol. 8 (4): 21 (1921). C. A. 16: 2405 (1922).
- 11. H. Sandquist, Ing. Vetenspaps. Akad. Handl. No. 10 (1922).
- 12. Kiefernol (Liquid rosin, poly terpen, sulfatharz) by Hakan Sandquist, Papier-Fabr. 20, (50): 1713 (Dec. 17, 1922).
- 13. Process for the conversion of tall oil into technically useful products, by Josef Ziv, Ger. Pat. 494,950 (June 9, 1923), C. A. 24, 3670 (July 20, 1930).

- 14. Experiments with sulphate soap and sulphate oil (floating resin), by
  H. E. Wahlberg. Svensk. Papers.-Tid. 27:168-9 (1924). C.A. 18:
  2409 (1924)
- 15. Hardened fatty products from liquid resin, by H. O. V. Bergstrom. Swed. Pat. 57,226 (Sept. 3, 1924).
- 16. Aqueous emulsions of solutions of tall oil, by Hein and Comp. Ger. Pat. 479,085 (June 10, 1925); C.A. 23: 4842 (1929).
- 17. Fatty acids in pine oil, by T. Hasselstrom. Paper Trade J. 83 (2): 60-64 (July 8, 1926); Papers och Travarutiskrift (Finland) (22): 632 (1925) Abs. in Paper Trade J. 84, (15): 49 (April 14, 1927). Finish Pat. 11,469 (November 26, 1925). Finnish Pat. 11,455 (November 23, 1925).
- 18. Harz der Nadelholzer, by R. Sieber, Verlag der Papier Ztg. Berlin 1925.
- 19. Rosin from oulp mill black liquor, by F. E. Greenwood. U. S. Pat. 1,560, 20 (Nov. 3, 1925): C.A. 20, 290 (1926).
- 20. Tall oil (properties of), by Duesberg, Seifensieder-Ztg. 52, 873 (1925); C.A. 20, 514 (1926).
- 21. Composition and utilization of tallol, by Maurice De Keghel. Rev. chim. ind. 35, 170 (1926); C.A. 21, 1354, (1927),
- 22. Method for separating solid, resin-like compounds and oily fatty acids from tall oil. H. Nordlinger, Chemische Fabrik. Florsheim A. G. Ger. Pat. 434,924 (1926).
- 23. Preparation of fatty acid compounds, by A. Riebecksche Montan-werke A. G. Ger. 429,272 (1926).
- 24. Process for obtaining fatty acids from raw tall oil, by Oel-und fett Chemie G. m. b. h. Magdeburg. Ger. Pat. 484,243 (Oct. 12, 1926); Brit. Pat. 278,697 (Oct. 11, 1926); C. A. 24, 984 (Feb. 20, 1930).
- 25. Purification of liquid rosin. Papier-Fabri. 24, 180 (March 21, 1926);
  Paper Trade J. 83, (2):60 (July 8, 1926), Ab. in Paper Trade J. 83, (15):49 (April 14, 1927); C. A. 20, 3566 (1926).
- 26. Tall oil, a byproduct of sulphate pulp mfg., by M. Ditmer. Z. angew. chem. 39, 262, (1926); C. A. 20, 2072 (1926).
- 27. Tall oil products. (Oel- und fett chemie G.m.b.h.) Ger. Pat. 477,829 (Dec. 5, 1926). Nor. Pat. 45,894 (Nov. 11, 1927); C.A. 23, 4842 (1929).
- 28. Treating pulpmill black liquor, by F. E. Greenwood. U. S. Pat. 1,593,656 (July 27, 1926); C.A. 20, 3236 (1926).

- 29. Treating tall oil. A. Schultze and co. Brit. Pat. 281,637 (Dec. 4, 1926); C.A. 22, 3529 (1928).
- 30. Composition and utilization of tall oil, by M. De Keghel. Pulp and Paper Mag. Canada 26, (16):529, 546 (April 19, 1928); C.A. 21, 1352 (1927); 22, 3295 (1928); Paper Trade J. 85, (21):50 (Nov. 24, 1927); abs. Paper Trade J. 87 (10):71 (Sept. 6, 1928).
- 31. Residual oils. Oel.-und Fett-chemie. G.m.b.h. French Pat. 643,853 (Nov.15, 1927); C.A. 23, 1750 (1929).
- 32. Manufacture of floating soap, by C. H. Michelson. Finn. Pat. 12,689 (May 9, 1928).
- 33. Purifying oils, by Soc. Meusienne de Prod. Chim. Fr. Pat. 656,728 (June 29, 1928); C.A. 23, 4343 (1929). Fr. Pat. 663,728 (Jan. 5, 1929).
- 34. Recovery resinous products in wood pulp mfg., by E. H. French. U.S. Pat. 1,693,586 (Nov.27, 1928); C.A. 23, 722 (1929).
- 35. Recovery of resins from black liquors, by K. G. Bergstrom. Fr. Pat. 663,416 (Feb. 6, 1928); C.A. 24, 739 (1930).
- 36. Process for the recovery of phytosterin, fatty and resinic acids obtained from raw sulphate soap as byproducts in the manufacture of sulphate soap. Satt att utvinna fytosterin, fettsyror och hartssyror ur ra sulfatsapa, by H. Sandqvist and T. O. H. Lindstrom. Swed. Pat. 80,941 (March 22, 1928).
- 37. Use of tallol (liquid rosin) in the alkali wash of petroleum disstillate, by K. Dittler, Chem.-Ztg. 52, 577 (1928); C.A. 22, 4238 (1928); abs. Paper Trade J. 89, (8):80 (August 22, 1929).
- 38. Working up cellulose industry byproducts, by C. H. Michelson. Ger. Pat. 503,030 (July 27, 1928); C.A. 24, 5157 (1930).
- 39. Process for treating talloel, by Willi Schultze. U.S. Pat. 1,736,802 Nov. 26, 1929; C.A. 24, 744 (1930).
- 40. Recovery of resin. Soc. chim. des resins du pin. Nor. Pat. 47,181 (Feb. 4, 1929).
- 41. Phytosterol from sulphate soap, by Ewald Pyhala. Acta Chem. Fennica 3, (10, 12):125 (Dec. 15, 1930).
- 42. Rosin soap material from spent wood liquors, by Viggo Drewsen. U.S. Pat. 1,778,523 (Oct. 14, 1930); C.A. 24, 6016 (1930).
- 43. Valuable constituents of sulphate soap, by H. Sandqvist and T. H. Lindstrom. Tekn. Tidskr., Chemie 60, 41 (1930).

- 44. Liquid resin and its possible uses, by W. Schmid. Papier-Fabr. 29, (1):1 (Jan. 4, 1931); abs. Paper Trade J. 92, (20)62 (May 14, 1931); Zellstoff u. Papier 13, (12):571 (Dec. 1933); C.A. 28, 2529 (1934).
- 45. Method of treating talloel, by Willi Schultze. U.S. Pat. 1,826,224 Oct. 6, 1931. Paper Trade J. 95, (2):29 T.S.15. (July 14, 1932); C.A.26, 613 (1932).
- 46. Process for the distillation of floating rosin precipitated as a byproduct in the manufacture of sulphate soap, by E. Oeman. Stocksund. Finn. Pat. 15, 731 (Feb. 27, 1931).
- 47. Process of recovering resinous byproducts in the manufacture of wood pulp, by E.H.French. U.S. Pat. 1,810,472 (June 16,1931); C.A. 25, 4708 (1931).
- 48. Process for working up tall oil, by Robert Held and Hans Franzen.
  Ger. Pat. 578,843 (Nov. 6, 1931); C.A. 28, 922, (Feb. 10, 1934).
- 49. Refining of "soap" floating on the waste liquors of cellulose manufacture, by C.H. Michelson. U.S. Pat. 1,823,752 (Sept. 15, 1931); C.A. 26, 305 (1932).
- 50. Sulphate black liquor soap disposal, TAPPI Special Report No. 152, (April 10, 1931).
- 51. Tall oil and its possible uses, W. Schmid, Farben-Chemiken 2, 306 (1931) Cf. C.A. 25, 3165 (1931); C.A. 25, 5582 (1931). Papier-Fabr. 29, (1);1 (Jan. 4, 1931); C.A. 25, 3165 (1931); Paper Ind. 12, 2117 (1931).
- 52. Use of tall oil as core binders. Imp. Chem. Ind. Ltd. and H. M. Bunbury. Eng. Pat. 348,315 (May 14,1931); C.A. 26, 3087 (1932).
- 53. Compositions adapted for use as emulsifying agents, by Imp. Chem. Industries Ltd. Lond., H. M. Bunbury, and R.P.McGlynn. Eng. Pat. 369,985 (Mar. 29, 1932). C.A. 27, 3046 (1933).
- 54. Process for the continuous manufacture of liquid rosin from raw soap obtained as a byproduct in the manufacture of sulphate pulp.

  H. Bergstrom and K. Cedarquist. Swedish Pat. 87, 842 (Sept. 8, 1932). Abs. Paper Trade J. 106(8):136 T.S. 88 (Feb. 24, 1938).
- 55. Process for the mfg. of material from pine oil for floor and wall covering, "Deutsche Lineoleum werke, A.G. Berlin." Swed. Pat. 80,570 (Feb. 8, 1932). Abs. Paper Trade J. 101, (7):45, (August 15, 1935.)
- 56. Process for the preparation of "soft soap" from so-called "floating rosin" as a byproduct in the manufacture of sulphate pulp, by A. Hellstrom. Nor. Pat. 52,815 (Oct. 28, 1932); Abs. Paper Trade J. 98, (22):33, (May 31, 1934).

- 57. Process of recovering rosin from rosin containing soap produced in the mfg. of paper from rosin containing wood, by L.N. Bent. U.S. Pat. 1,888,581 (Nov. 22, 1932); C.A. 27, 1503 (1933).
- 58. Process for refining and discoloring of raw sulphate soft soap, by Ewald Pyhala. U.S. Pat. 1,887,246 (Nov. 8, 1932).
- 59. Refining liquid rosin, by H. Bergström. Svensk. Papers-Tidn. 35, (5): 156, 161 (March 15, 1932); C. A. 26, 3124 (1932).
- 60. Tall oil distillate in soaps, by G. Knugger. Seifensieder Ztg. 59, 782 (1932); C.A. 27, 1224 (1933).
- 61. Cellulose turpentine, by A. H. Weissner. Farbe u. Lack. 261 (1933); C.A. 27, 4073 (1933).
- 62. Centrifugal separator for the removal of fats, soaps, and resins from diffuser black liquors, by S. D. Wells. U.S. Pat 1,934,957 (Nov. 14, 1933); Abs. Paper Trade J. 98 (22):33 (May 31, 1934).
- 63. Distribution of the sulphate soap during the washing of the diffusers, by Bergström and Cederquist. Svenske Papers-Tidn. 38 (17):571 (Sept. 15, 1933); Abs. Paper Trade J. 103 (5):32 (July 30, 1936).
- 64. Method of obtaining phytosterol fatty acids and resin acids from raw soap or liquid resin obtained in the manufacture of cellulose according to the sulphate method, by Sandqvist, Hakan. U.S. Pat. 1,940,372 (Dec. 19, 1933); C.A. 28, 1533 (1934).
- 65. Method of polymerizing, condensing, and oxidizing tall oil and the resulting product, by R. H. Patch and F. Dambacher, U. S. Pat. 1,938,532 (Dec. 5, 1933); C.A. 28, 1207 (1934).
- 66. Production of valuable products from tall oil, by Hans Franzen and Robert Held, U.S. Pat 1,921,556 (Aug. 8, 1933); C.A. 27, 5207 (1933)
- 67. Recovering rosin from crude collected mixtures, by A.R. Hitch and I. A. Ebaugh. U.S. Pat.1,899,388 (Feb. 28, 1933); C.A. 27, 3094 (1933)
- 68. Sulphonated derivatives of tall oil, by J.R. Geigy. A.G. Swiss Pat. 156,113; C.A. 27, 1212 (1933).
- 69. Black soap and sulphate black liquor, by Ewald Pyhala. Mat. Grasses 26, 10,290, 10,317 (Oct. Nov. 1934); C.A. 29, 3831 (1935).
- 70. Liquid Resin (Tall oil), R. Klatt. Fett chem. Umschau 41, 90 (1934); C.A. 28, 4901 (1934).
- 71. The development of different methods for purifying the raw sulphate rosin soap, by E. Pyhala, Zell. u. Papier 14, (7):273 (July 1934); Abs. Paper Trade J. 101, (7):45 (Aug. 15, 1935).

- 72. The quantity of liquid rosin obtained in sulphate cooking vs. resinic acid and fatty content of the wood, by H. Bergström and K. Cederquist. Iva 2, 42 (1934); C.A. 28, 4595 (1934), Abs. Paper Trade J. 99 (19): 240 (Nov. 8, 1934).
- 73. Use of tall oil in soap making. A Lamanovich and N. Fret'Yakova-Masloboino Thirova Delo. 10, (12):39 (1934); C. A. 29, 8379 (1935).
- 74. Making soap from wood, by A. Hellstrom, Paper Ind. 17,(3):173 (June 1935).
- 75. Production of pure byproducts from resin-containing liquors, by E. H. French, U. S. Pat. 1,997,171 (April 9, 1935); C.A. 29, 3864 (1935).
- 76. Refined sulphate black liquor, talloel and process of making the same, by Torsten Hosselstrom, U. S. Pat. 1,986,815 (Jan. 8, 1935); C.A. 29, 1249 (1935).
- 77. The raw material problem of the German soap industry, by R. Krings. Seifensieder-Ztg. 62, 115 (1935); C.A. 29, 3185 (1935).
- 78. Use of liquid resin (tall oil) in soap making, by Kuptschvisku and A. Yasnui. Maslob. Zhir. Delo. 11, 492 (1935); B.C.A. 585, (1937B) C.A. 30, 893 (1936).
- 79. Use of the waste from rosin soap preparation in the paper industry, by P.D. Sotov, Bumazhnaya Prom. 14, (9):45, (Sept. 1935).
- 80. Water soluble resinate production, by E. H. French. U.S. Pat. 2,012,125 (August 20, 1935); C.A. 29, 6782 (1935).
- 81. A new method for refining tall oil II, by R. H. McKee and H. L. Bleugsli, Paper Trade J. 103, (14):33 (Oct. 1, 1936); C.A. 30 (8613) (1936).
- 82. Dehydrogenation of liquid resin, by H. O. V. Bergstrom and K. M. Cederquist. Swed. Pat. 86,321; C.A. 30, 8666 (1936).
- 83. Historical development of the tall oil industry I, by R. H. McKee and H. L. Bleugsli. Paper Trade J. 103, (12):34 (Sept. 17, 1936); C.A. 30, 8613 (1936).
- 84. Phthalic acid glycerol tall oil resins, by F. Kalke. Farben-Ztg. 42, 942 (Sept. 18, 1936); C.A. 31, 3308 (1937).
- 85. Recovery of waste products at the Lobov Salombal'sk sulphate pulp mill, by G. S. Kovalevich. Bumazhnaya Prom. 15, No. 10, 20 (Oct. 1936); C.A. 31, 2422 (1937); Abs. Paper Trade J. 105, (21):38 (Nov. 18, 1937.)
- 86. Tall oil as a varnish material, by H. Reinert, Farbe u. Lack. 461 (1936); C.A. 31, 5603 (1937).

- 87. Tall oil, by R. Fussteig. Mat. grasses 28:10768-10769 (1936).
- 88. Tall oil fat acids. Fr. Kolke. Farben-Ztg. 41:1186 (1936); C.A. 31: 3308 (1937); Paper Trade J. 106 (4):36, T.S. 32 (Jan. 27, 1938).
- 89. Tall oil liquid rosin, by C. Becher. Chem.-Ztg. 60, No. 37, 373 (May 6, 1936); Abs. Paper Trade J. 103, (15):40 (Oct. 8, 1936).
- 90. Uses of tall oil. Tech. Bull. Paper Makers Assoc. Gt Britain and Ireland 13 (8):109 (August 1936); Abs. Paper Trade J. 103 (23):44 (Dec. 3, 1936).
- 91. Einrichtung zum verbinden zweier teile von gegenständen, by Georg Hossenfelder. Berlin, Karl Lenck (1937).
- 92. Fatty acids from pine wood, by J. A. Wallach, Soap 13, (3):31-33, 73 (1937); C.A. 31, 3313 (1937); Abs. Paper Trade J. 106(4):36 (Jan. 27, 1938).
- 93. Liquid rosin is being produced in greater quantities in Europe.
  Naval Stores Rev. 47, (5):10 (May 1, 1937).
- 94. Manufacture of sized papers. Oscar F. Neitzke (Bennett, Inc).
  U.S. Pat. 2,093,337 (Sept. 14, 1937); Abs. Paper Trade J. 106 (9):
  28, T.S. 154 (March 3, 1938).
- 95. Occurrence of resin acids in black liquor and wash water, by
  Bergström, Hilding, and Cederquist. Svensk Pappers-Tidn. 40
  (5):112 (March 15, 1937); C.A. 31, 4114 (1937); B. I. P. C. 7:295;
  Abs. Paper Trade J. 106 (4):36 (Jan. 27, 1938).
- 96. Pine stumps to fine chemicals, by R. C. Palmer. DuPont Mag. 31 (4):18-20, 24, (April 1937).
- 97. Tall oil fat acids with regard to chemistry and paint technology, by
  H. Heller. Fette u. Seifen 44, 486 (1937); C.A. 32, 1121 (1938);
  Abs. Paper Trade J. 106 (21):45 (May 26, 1938).
- 98. Tall oil fat acids with regard to chemistry and technology, by
  H. Niesen. Fette u. Seifen 44, 426 (1937); C.A. 32, 1121 (1938);
  Abs. Paper Trade J. 106 (21):45 (May 26, 1938).

#### Manufacture

Liquid rosin is a byproduct obtained in the manufacture of sulphate pulp from pine (pine = "tall" in Swedish), hence the name "Tall-Oil" that is often used in as a commercial term. A soap is separated from the waste liquor and the liquid rosin is obtained from the soap through precipitation with sulphuric acid or sodium bi-sulphate solution.

#### Constituents

The composition of liquid rosin is not constant due to variations in the contents of resinous and fatty acids in the wood. Ordinary liquid rosin usually tests as follows:

	Percent
Water	0.5 - 2.0
Unsaponifiable matters	8.0 -11.0
Resinous acids	35.0 -45.0
Fatty acids	45.0 -55.0

Usually it is sold as about 90 percent saponifiable.

Liquid rosin is a dark-brown and thickish oil, at times somewhat cloudy and at times with a sediment of small crystals of resin. Due to certain sulphurous matters it has a characteristic smell.

### Purification

The smell can be improved to a high degree through treatment with oxidating agents or through partial hydration.

Usually the rosin is, however, purified through distillation in vacuum with or without steam. It is then divided into the following fractions:

	Abt.	Percent
Fuel-oil	• •	5
Fatty acids (refined tall-oil)		45
Solid rosin		20
Pitch	• •	30

The quantities of these distillation products, as well as the quality, vary according to the composition of the crude rosin and the manner in which the distillation has been carried out.

The products obtained by distilling crude rosin have all found their uses.

This product still contains some resinous acids but it consists mainly of fatty acids such as palmitic, oleic and linoleic acid. The refined tall-oil is light-yellow in color and is free from disagreeable smell. It is used in the manufacture of hard and soft soap. It can be transferred into solid fatty acids by hydration and can be used to substitute more expensive vegetable and animal fats. An oil of linseed oil type can be produced through esterification with glycerine. After a sickative is added it will dry easily and can be used as a substitute for linseed oil in the manufacture of varnish. Such esterified tall-oil is for sale in Germany.

The rosin obtained through distillation comes in crystalline form but can be transferred into an amorf state by smelting. It is very similar to ordinary colophonium, but the melting point is somewhat higher. It can be used to advantage in the manufacture of rosin-size, especially according to the Delthirna method.

The pitch obtained by distillation varies in composition depending upon the point to which the distillation has been carried out. It has found many uses such as for lac-varnish and in the manufacture of printers ink. It is also used as a substitute for asphalt in road building and for similar purposes.

Liquid rosin is used without purification for several purposes, such as asphalt emulsions for road building. Other uses for liquid rosin, as well as for the distillation products, are as oil for moulding cores, bore-oil and disinfectants, also for impregnation and in the manufacture of washing soap for sheep and cattle.

A very valuable ingredient of liquid rosin (2-3 percent) is phytosterine, an alcoholic compound of high molecular weight, which generally is found in animal and vegetable fats. Phytosterine can be obtained in crystalline form and is an extremely good agent for emulgation of vaseline, grease etc., so it ought to find a considerable use for medicinal and cosmetic purposes as well as in the manufacture of marina oil. The possibility of using phytosterine, in a purified state, in the manufacture of vitamine and hormon preparations is not precluded.

-- Swedish Wood Pulp Journal, December 31, 1937.