for cineol. To the well-cooled oil, glacial phosphoric acid was slowly added according to Scammell's process.¹ After decanting as much of the oil as possible the magma was placed in a Büchner filter, the filter placed in a centrifuge cup and centrifuged; in this way we were able to get the magma fairly dry without the loss of any of the adhering oil. After decomposition of the phosphate with hot water, a pure oil was obtained, which melted at -1°C . The cineol thus obtained constituted 30 per cent of the whole. The cineol was also identified by the formation of the iodol which, after recrystallization from benzene, melted at $111-112^{\circ}$.

The oil remaining in Fractions 3 to 7 after the removal of the cineol constituted approximately 25 per cent of the whole. This part of the oil was optically inactive and the boiling point and specific gravity indicated either terpinene or dipentene. An attempt was made to form the dipentene tetrabromide, but although crystals separated they were not in sufficient quantity to be identified. On treatment of the oil with Beckmann's reagent² (30 parts water, 6 parts potassium dichromate and 5 parts sulfuric acid), a heavy brown precipitate separated which showed that a considerable portion of the oil consisted of terpinene.

Fractions 8, 9 and 10 were subjected to a freezing mixture of ice and hydrochloric acid, a temperature -20° being attained. Solid crystals amounting to 25 per cent of the total oil separated. After the first sublimation these crystals showed slight optical activity, but after the second sublimation were optically inactive. They melted at 173°C . Pure camphor melts at 175° . The semicarbazone prepared according to the method of Tiemann,³ melted at 232° . The semicarbazone of camphor melts at $236-238^{\circ}$. Undoubtedly these crystals were camphor. After the removal of the camphor there remained approximately 10 to 12 per cent of the original oil. The boiling point was 200°C ., specific gravity 0.917, and specific rotation about 25.9° . To a solution of the oil in petroleum ether, bromine was slowly added according to the method of Wallach⁴ for preparing thujone tribromide; crystals were obtained which, after twice recrystallization from ethyl acetate, melted at $123-124^{\circ}$. Thujone tribromide melts at 122° .

A small quantity of oily substance remained from Fractions 8, 9 and 10 after the separation of the camphor and thujone; this was a resinous oil, probably partly formed by polymerization during the process of distillation, and partly consisting of other high boiling terpenes which occurred in quantities too small to be definitely determined.

	Analysis by Bureau of Plant Industry	Our analysis
1 Pinene.....	?	6.0 per cent
2 Cineol.....	22.5 per cent	30.0 per cent
3 Dipentene, terpinene, etc.....	?	25.0 per cent
4 Thujone.....	Trace	8.0 per cent
5 Camphor.....	40.0 per cent	25.0 per cent
6 Resinous material.....	?	5.0 per cent

A comparison of our analysis with that of the Bureau

of Plant Industry gives a good indication as to the variation of the constituents of the oil with the season.

At the earlier season at which we obtained our material, the oil contains a considerably higher percentage of the lower boiling constituents, while at the later period a somewhat greater percentage of camphor was found.

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EXAMINATION OF CHINESE WOOD OIL¹

By E. E. WARE AND C. L. SCHUMANN

The use of Chinese wood oil as a varnish oil, although of fairly recent adoption, except in the Orient, has increased rapidly until at the present time wood oil has come to be considered the important oil of the varnish industry.

The value of the oil has been said to lie in its ability to form actual combinations with the abietic acid of the rosin with which it is cooked. This statement may be open to question, but the fact remains that varnishes of superior quality can be made from wood oil and rosin when they are properly manipulated.

Most of the Chinese wood oil imported into the United States is gathered in small quantities throughout the rural districts of western China, and after passing through the hands of several native collectors and dealers, reaches Hankow, where it is put into the export packages. The American buyer, although reasonably certain that he receives the oil as packed at Hankow, has no assurance that the oil he buys is representative of the oil as pressed from the nut. The wide variations that the varnish-maker finds in the oil as he uses it may be due to variations in the nut and in its treatment, or to adulteration by one or more of the various middlemen during its open-basket travel from interior China to the forwarder's warehouse at Hankow.

METHODS OF EXAMINATION

Numerous methods have been proposed for the determination of the relative purity of wood-oil samples. Polymerization of the oil by heating at a definite temperature for a definite length of time, various modifications of which treatment have been proposed by Bacon, Worstall, Potsdamer, Browne, and others,² is the method in most general use at the present time. This method seems to have given the most satisfaction, since the analytical constants of wood oil vary within rather wide limits, and this variation does not seem to be accompanied by a corresponding variation in the working qualities of the oil, as judged by its action in the varnish kettle.

However, many buyers prefer to depend upon the analytical constants in passing judgment on wood oil, claiming that the personal equation has too strong an influence on the results obtained by the heat polymerization method. The iodine number and the re-

¹ U. S. Pharm., 1900, p. 313.

² Baeyer, *Ber.*, 27, 815.

³ Tiemann, *Ibid.*, 28, 2191.

⁴ *Ann.*, 275, 196; 286, 129.

¹ Presented at the 17th Annual Meeting of the American Society for Testing Materials, Atlantic City, June 30 to July 3, 1914.

² Boughton, "Testing of Chinese Wood Oil," *Proceedings Am. Soc. Test. Mats.*, 13 (1913), 923.

fractive index¹ seem to be the most reliable constants to use.

McIlhiney² offers a method for the examination of this oil that promises well when standardized. He precipitates the insoluble iodine addition products formed when wood oil is treated with iodine in acetic acid solution, and weighs the oil remaining after evaporation of the solvent from the filtrate.

LIGHT BREAK

A familiar characteristic that seems to have been neglected in the consideration of methods for judging the purity of wood-oil samples, is the light "break." It is a well-known fact that wood oil exposed to the light in bulk soon exhibits a flocculent white precipitate, which continually increases in amount until, after some months, the oil seems to be a solid white mass. This change in wood oil upon exposure to light is reported by Normann³ to be a polymerization. Fahrion⁴ does not agree with this view but calls the change a molecular transformation. Normann also finds that light has a similar effect upon the potash soap of Chinese wood oil and that the transformation takes place more rapidly than with the oil.

This break caused by sunlight seems to be characteristic of wood oil alone, and seems to be capable of standardization to the point that permits its use as an analytical method for the estimation of the purity of wood-oil samples.

The authors in studying this phenomenon have made use of certain catalytic agents that markedly influence the rate of transformation. Among these are iodine, sulfur,⁵ hydriodic acid, sulfur chloride, carbon dioxide, hydrogen sulfide, phosphorus tribromide, and carbon bisulfide.⁶ These agents act at different rates, and bring to completion, in times varying from a few hours to several weeks, a reaction that Morrell⁷ reports as proceeding only to the extent of 6 per cent in one year. Sulfur chloride and iodine are the only accelerators studied that will cause a complete precipitation within the time that permits the operation to be classed as an analytical method. Others of the catalyzers might be used as a means of getting a less contaminated product for the examination of its characteristics.

The action of sulfur chloride upon the drying and semi-drying oils is common knowledge. Jenkins⁸ reports the fact that sulfur chloride added to wood oil to the extent of 20 per cent will yield a jelly-like mass. The reaction is accompanied by an evolution of hydrochloric acid and considerable heat. Chinese wood oil is not alone in exhibiting this characteristic, some of the semi-drying oils showing quite as energetic an action toward sulfur chloride. The fact that such compounds are formed may not therefore be accepted as a test for the purity of wood oil. Gardner⁹ suggests

that as Chinese wood oil in carbon tetrachloride solution will form this addition product much more rapidly than will other oils under the same conditions, the action might be susceptible to a time standardization.

If the wood oil be thinned with a solvent upon which the sulfur chloride will not act, and the dilution be to a strength of solution of 20 per cent or less, the sulfur chloride then becomes merely a catalytic agent for the transformation of the wood oil by light, and there seems to be very little if any addition product formed. The oil will break to a considerable extent even in the dark, but the reaction is very much more rapid if exposed to light. If the concentration of the sulfur chloride be low and the mass cool, the reaction will proceed until within a few hours the oil is of the consistency of lard. In order that the reaction proceed to completion it is necessary that the break be filtered out at intervals.

The reaction between Chinese wood oil and iodine has been used as a qualitative,¹ and the modification introduced by McIlhiney as a quantitative method for the estimation of the purity of wood oil. If we carry the thinning still further than is recommended by McIlhiney, and use petroleum ether instead of glacial acetic acid, the addition of 0.3 per cent of iodine will give practically no additional products, but will accelerate the transformation of the oil into the insoluble elaeostearic glyceride of Fahrion.

ANALYTICAL METHOD NO. 1—The authors' procedure is as follows: Five grams of the oil to be examined are weighed into a small beaker, thinned with 25 cc. of petroleum ether (60° C. b. p.), and the whole cooled to 0° C. After cooling, 5 cc. of ice-cold, saturated solution of iodine in petroleum ether are added with stirring. Precipitation starts within a few minutes; the better the light the quicker the precipitation. After about 1 hour, more petroleum ether is added and the mass stirred thoroughly. The first filtration should take place after about 3 hours, the precipitation having proceeded by that time to show a conversion of about 50 per cent of the wood oil present. Little is gained by waiting longer before filtering, as the precipitate is so heavy as to mask the further action of light upon the oil. The filtrate from the first filtration is cooled and again exposed to light. A few milligrams of iodine in solution may be added at this point if the solution has become colorless. Three precipitations with the corresponding filtrations are generally sufficient to give total yield. The solution should be kept cold at all times during precipitation, although after each filtration the extra petroleum ether may be evaporated on the steam bath, if the solution be thoroughly cooled before the further addition of iodine and the exposure to light.

The material taken out by the third filtration is of somewhat different character from that precipitated earlier in the operation. This may indicate the presence of a third glyceride as a constituent of wood oil, and may account for the difference of opinion between Cloez,² who claims 75 per cent elaeomargaric acid and

¹ Wise, *THIS JOURNAL*, **4** (1912), 497.

² *Ibid.*, **4** (1912), 496.

³ *Chem. Ztg.*, **31** (1907), 186.

⁴ *Chem. Centrbl.*, **83** (1912), 2154.

⁵ Maquenne, *Compt. rend.*, **135** (1902), 696.

⁶ Andes, "Iron Corrosion and Anti-Corrosive Paints," p. 156.

⁷ *Transactions Chem. Soc.*, **101** (1912), 2082.

⁸ *J. Soc. Chem. Ind.*, **16** (1897), 195.

⁹ *Proceedings Am. Soc. Test. Mats.*, **13** (1913), 946.

¹ Boughton, *J. Soc. Chem. Ind.*, **28** (1909), 719.

² *Compt. rend.*, **81** (1875), 469.

25 per cent oleic acid, and Fahrion¹ who finds 90 per cent and 10 per cent.

In Table I are compiled the data obtained by the

TABLE I—EXAMINATION BY PRECIPITATION OF LIGHT BREAK

SAMPLE No.	G.	ADULTERANT G.	Kind	Residue G.	Oil precipitated due to residue		ADULTERANT		
					calculated %	calculated as % g.	Calculated G.	Present %	Found %
1	5.000	...	...	0.365	92.7	0.350	0.015	0.0	0.3
1	5.035	...	...	0.415	91.8	0.353	0.062	0.0	1.2
1	5.440	1.010	Sesame	1.335	94.0	0.381	0.954	15.7	14.8
1	5.160	1.000	Sesame	1.400	92.2	0.361	1.039	16.2	16.9
1	5.040	0.580	Sesame	0.920	93.3	0.353	0.567	10.3	10.1
1	5.120	0.500	...	0.815	93.8	0.358	0.457	8.9	8.2
1	5.030	1.040	...	1.400	92.8	0.352	1.048	17.2	17.3
1	5.010	1.010	...	1.330	93.6	0.357	0.973	16.8	16.1
1	4.945	1.665	Soya bean	1.920	94.8	0.346	1.574	25.2	23.8
1	6.680	0.420	...	0.940	92.2	0.468	0.472	5.9	6.6
1	5.180	0.495	...	0.825	93.6	0.363	0.462	8.7	8.1
1	5.040	0.280	...	0.650	93.1	0.353	0.297	5.3	5.6
1	6.810	1.150	...	1.470	95.3	0.477	0.993	14.5	12.5
2	5.130	...	...	0.320	93.6	0.359	-0.039	0.0	-0.6
2	5.135	...	...	0.360	93.0	0.360	0.000	0.0	0.0
3	5.135	...	...	0.300	94.1	0.360	-0.060	0.0	-1.1
3	5.600	...	...	0.360	93.6	0.392	-0.032	0.0	-0.6

NOTE—Wood oil No. 1 was furnished by the Acme White Lead and Color Works, and is a Hankow oil of high quality. Wood oils Nos. 2 and 3 are the standard oils from the American Society for Testing Materials, and were furnished through the courtesy of Mr. H. A. Gardner and Mr. L. P. Nemzek.

use of this method in the examination of several Chinese wood oils and of other samples in which these oils were mixed with varying amounts of sesame and soya bean oil. The figures in the column entitled "Adulterant (calculated)" were obtained as the difference between the actual weight of the residue and the calculated weight, using 7 per cent of the weight of the wood oil in the sample as the average weight of residue obtained from pure oil. In cases where the figures show negative, indicating an actual weight less than the calculated, the figures were inserted merely to show the extent to which the inaccuracy of the method is apparent.

The results in Table I indicate a precipitation of approximately 93 per cent of the wood oil present, when using iodine as a catalyzer. Sulfur chloride does not seem to be so efficient in its action upon the raw oils. The precipitation proceeds at a slower rate, and there seems to be a strong tendency for the material to skin over with an oxidized film during the precipitation. No quantitative results on sulfur chloride precipitation are included in the table.

The method of estimation used in arriving at the figures given in Table I is the weighing of the final filtrate after evaporation of the petroleum ether. The amount of adulteration may be considered as the weight of the filtrate minus the amount of the residue due to the unprecipitated olein present in the wood oil. This amount of unprecipitable matter has been taken as 7 per cent of the wood oil, that amount having been shown to be an average for a number of determinations on supposedly pure wood oil.

It is possible to get an estimation of the amount of wood oil present by the direct weighing of the precipitated matter. In that case great care must be exercised to prevent oxidation of this material during drying.

The tabulated results show the possibilities of this method as a means of detecting adulteration in wood oil. It is certain that further refinement of the method is possible, which will add to its accuracy.

INSOLUBLE SOAP

In studying the characteristics of this solid precipitated glyceride, it was noted that the potassium soap was but slightly soluble in absolute alcohol, which agrees with the findings of Normann¹ and Morrell² who worked on the material precipitated by sunlight alone. Morrell, however, also states that the soap is practically insoluble in water, which statement is not borne out by the experience of the authors.

The comparative insolubility of the potassium soap of Chinese wood oil offers possibilities of a rapid method for the detection of adulteration in wood-oil samples. The saponified product separates quite completely from absolute alcoholic potash, and may be washed free from the soap of the adulterating material. If the method be carried out at uniform temperature, preferably 0° C., and the alcohol for washing the precipitate be previously saturated with the soap, it is possible to estimate the amount of adulteration within fairly narrow limits.

ANALYTICAL METHOD NO. 2—A 3-g. sample of the oil to be examined is saponified with 100 cc. of *N*/4 absolute alcoholic potash for one-half hour, using an air condenser of sufficient length to prevent the loss of alcohol. The saponified mixture is cooled to 0° C., held for 10 minutes at that temperature, and filtered through a Gooch crucible using a filter-paper disk instead of an asbestos pad. The precipitate, after washing thoroughly with ice-cold saturated absolute alcohol, is removed from the crucible to a cover glass, and is dried at 75 to 80° C., under vacuum, and with a stream of dry hydrogen or carbon dioxide passing through the desiccator. After cooling without removing from the desiccator, the precipitate is taken out and weighed, and the weight calculated to wood oil.

It is necessary, if the method is to be at all accurate, to use absolute alcohol both for saponification and for washing the precipitate, as the soap is appreciably soluble in the presence of even small amounts of water. This alcohol and alcoholic potash should be freshly saturated with the soap before use, for although the soap is but slightly soluble in absolute alcohol, that solubility changes on standing, especially if exposed to light. It is a comparatively easy matter to keep freshly saturated solutions ready for use by making up a batch of the soap and introducing it into the stock bottles of alcohol and alcoholic potash, in quantities more than sufficient to saturate them at 0° C. When about to make a determination, the solution may be warmed until an appreciable amount of soap goes into solution, after which it may be cooled to 0° C. and held for 10 minutes and filtered. This fresh filtrate is ready for use, and the fact that the procedure followed will be duplicated on the saponified sample helps to insure the accuracy of the determination.

During the washing of the precipitate the whole must be kept cold, for the solubility of the material in alcohol is greatly increased by a rise in temperature. This is accomplished by filtering through a Gooch crucible surrounded by cracked ice. The authors

¹ Chem. Ztg., **31** (1907), 188.

² Trans. Chem. Soc., **101** (1912), 2082.

have found the apparatus shown in Fig. I to be quite satisfactory.

The precipitate is susceptible to oxidation and must be kept away from air during drying. Also, the fact that high temperature will char the soap limits the drying temperature to about 80° C. The precipitate may be dried in a desiccator connected by a long rubber tubing to a source of hydrogen or carbon dioxide, and to a vacuum pump. After introducing the precipitate to be dried, the desiccator may be placed in a low-temperature steam drying oven for 3 hours.

The results obtained by the use of the insoluble-soap method and the data from which these results were computed, are compiled in Table II. In calculating the results for this table it was decided to accept the weight of the dried insoluble soap as representative of the weight of wood oil present in the sample, since the error of this assumption was considered to be within the limits of error of the method.

Although neither of the above methods has proved entirely satisfactory as a method for the estimation of wood oil in rosin varnishes, the efforts made to apply them to that end have resulted in some interesting data regarding the conditions existing in this type of varnish.

TABLE II—EXAMINATION BY PRECIPITATION OF INSOLUBLE POTASSIUM SOAP

SAMPLE No. G.	ADULTERANT		WOOD OIL		ADULTERANT		
	G.	Kind	Soap G.	Cal- cu- lated G.	Found		Present %
					G.	%	
1	3.301		3.334	3.334	101.0	—0.033	—1.0
1	2.814	0.304	2.807	2.807	99.8	0.311	9.9
1	3.012	0.180	3.021	3.021	100.3	0.171	5.5
1	2.516	0.506	2.508	2.508	99.8	0.514	17.0
1	3.138		3.170	3.170	101.0	—0.032	—1.0
1	2.859	0.959	2.874	2.874	100.6	0.944	24.7
1	2.642	0.881	2.645	2.645	100.1	0.878	24.9
1	3.013		3.006	3.006	99.8	0.007	0.2
1	3.006	0.167	2.982	2.982	99.2	0.191	6.0
1	2.051	1.302	2.020	2.020	98.1	1.333	39.8
1	2.461	0.125	2.536	2.536	103.0	—0.075	—2.9
1	2.791	0.607	2.883	2.883	103.3	0.515	15.2
1	2.742	0.380	2.761	2.761	100.7	0.361	11.5
1	2.742	0.183	2.741	2.741	100.0	0.184	6.3
1	2.528		2.501	2.501	98.9	0.027	1.1
1	2.524		2.550	2.550	101.0	—0.026	—1.0
1	2.521		2.510	2.510	99.5	0.011	0.5
1	2.510		2.514	2.514	100.2	—0.004	—0.2
1	2.321	0.707	2.367	2.367	102.0	0.661	21.8
1	2.428	0.738	2.508	2.508	103.3	0.658	20.8
1	3.019		3.019	3.019	100.0		
1	3.039	0.409	3.025	3.025	99.5	0.423	12.3
1	3.199	1.049	3.201	3.201	100.3	1.038	24.5
2	3.252		3.224	3.224	99.1	0.028	0.9
3	3.471		3.544	3.544	102.1	—0.073	—2.1
4	3.156		3.014	3.014	95.5	0.142	4.5
4	3.190		3.092	3.092	96.9	0.098	3.1

NOTE—Wood oils Nos. 1, 2 and 3 were the same as those in Table I. Wood oil No. 4 was furnished by Mr. L. P. Nemzek, representing the Educational Bureau of the Paint Manufacturers' Association. This oil is from American-grown nuts.

An examination of the separated constituents of a Chinese-wood-oil rosin varnish seems to show that the polymerization of wood oil in the presence of rosin is practically as complete as in the oil, subject to the same heat treatment in the absence of rosin. The fatty acid in each case shows a molecular weight double that of the fatty acid of raw wood oil. The difference in characteristics between these two polymerized products has not as yet been satisfactorily accounted for.

A comparison of the molecular weights of the fatty acids from raw wood oil and the light breaks seems to show that this light break is an isomer rather than a polymer, and that there is practically no difference between the light break formed slowly by sunlight alone and that catalyzed by iodine.

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OILS OF THE CONIFERAE. II—THE LEAF AND TWIG, AND BARK OILS OF WHITE FIR

By A. W. SCHORGER

Received August 15, 1914

The white fir [*Abies concolor* (Gord.) Parry] is found on the mountain slopes from southern Oregon to Lower California and from Nevada, Utah, and southern Colorado through Arizona and New Mexico. The dense crown consists of short, heavily foliated branches. The leaves at the top of the tree are usually 1 to 1½ inches in length, while those of the lower branches are somewhat longer—1½ to 3 inches.

LEAF AND TWIG OILS

The oils were greenish yellow in color with a green fluorescence with the exception of samples Nos. 2439 and 2487, which were lemon-yellow in color and showed no fluorescence. The residue left after removal of the terpenes by distillation was fluorescent to a marked degree, but this property was not noted in the "green oil" fraction obtained, though the oil owes its green color to this fraction.

The properties of the oils and the yields are given in Table I.

TABLE I—PROPERTIES OF OILS

Sample No.	d_{15}°	n_{D15}°	α_{D25}°	Acid Ester		Ester No. after acetyl-	Ace- tate Per cent	Per cent alcohol		Yield of oil Per cent
				No.	No.			Free	Total	
LEAF AND TWIG OILS										
2176	0.8758	1.4788	—27.94	1.13	12.52	48.88	4.38	10.28	13.73	0.140
2180	0.8738	1.4786	—20.18	1.81	27.34	54.58	9.57	7.65	15.17	0.029
2181	0.8732	1.4786	—21.65	1.43	24.03	52.45	8.41	7.99	14.60	0.050
2183	0.8737	1.4796	—26.87	1.07	20.55	54.22	7.19	9.50	15.15	0.150
2439	0.8720	1.4787	—26.59	1.01	14.48	51.83	5.07	10.57	14.55	0.163
2440	0.8745	1.4790	—24.08	1.32	14.80	47.84	5.18	9.32	13.39	0.095
2487	0.8777	1.4781	—20.11	1.06	18.79	55.51	6.58	10.39	15.56	0.272
Mean,							6.63	9.39	14.59	0.128
BARK OILS										
			α_{D20}°							
2209	0.8767	1.4833	—20.95	1.22	6.88	23.34	2.41	4.58	6.48	0.07
2423	0.8702	1.4809	—20.15	0.87	6.43	20.45	2.25	3.90	5.67	0.12
Mean,							2.33	4.24	6.08	0.095

There is a considerable variation in the ester and free alcohol content in the various samples but the total alcohol content is fairly uniform. Samples Nos. 2439 and 2440 were distilled from material taken from the top and base, respectively, of the same tree. The needles from the top of the tree show a slightly greater total alcohol content.

Six hundred grams of oil distilled as follows: 161–165°, 15.5 per cent; 165–170°, 42 per cent; 170–180°, 18.5 per cent; 180–195°, 3 per cent; 195–240°, 13 per cent; 240–310°, 3 per cent.

IDENTIFICATION OF CONSTITUENTS

FURFURAL—The first fraction was shaken out with water. On treating the aqueous extract with aniline and hydrochloric acid a deep crimson color characteristic of furfural was obtained.

α -PINENE—The fraction examined for α -pinene had